A STUDY OF THE ACTIVITIES OF CONSTITUENTS OF MOLTEN SLAGS.

THESIS

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by

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C O N T E N T S.

INTRODUCTION.

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With the accumulation of free energy data for a great number of reactions of interest in the extraction and refining of metals it is becoming possible to estimate the equilibrium positions for many of these reactions. Such positions are expressed in terms of activities of the reactants so that to make use of the data, the activity coefficients of the reactants must be found experimentally. In most cases this means establishing the coefficients for a wide range of concentration of the solute and in solvents of different compositions.

Such data are of importance for two main reasons. One reason is the need in industrial processes to decide whether or not any given reaction among several simultaneous reactions has reached equilibrium. The other reason is that activity coefficients shown by a constituent of a solution throws light on the question of the structure of such a solution.

Both of these points arise in iron-making in the blast furnace. Slag melts are very complex structures and study of their chemical behaviour in this way along with study of their physical properties will enlarge understanding of their nature.

The question of attainment of equilibrium is probably of more immediate practical importance and arises in many forms in iron-making. This is so because successful production of iron requires that the iron should fall within certain composition limits and, of course, be produced as cheaply as possible.

In iron produced for steelmaking, which constitutes the greatest part of iron-making, silicon and sulphur contents are the most important composition variables which are more or less within the control of the iron-maker. For basic open hearth steel production, which uses most of the iron produced, both sulphur and silicon content should be low. For acid bessemer steel production sulphur must be low and silicon content controlled to give sufficient heat for the process on oxidation to silica.

For neither of these constituents is the process which governs their final concentration in the metal fully understood. In both cases the state of oxidation of metal and slag has a part to play and this is governed to some extent at least and may be wholly, by the oxygen potential of the system carbon - carbon monoxide. The oxygen potential of the slag is related to the iron oxide content of the slag. Thus iron oxide content of the slag is an important factor in sulphur and silicon removal. Its significance can also be considered to lie in its possible reactions with silicon and sulphides.

The problem of silicon distribution is the more complicated and less well understood of the two and will be considered first.

It is still not known if silica reduction continues in the hearth or if silicon in iron produced by reduction of silica at high temperatures near the tuyere zone reduces iron oxide and manganese oxide in the slag and so helps to reduce the oxygen potential of the slag.

The probable reactions governing silicon distribution are:-

$$(SiO_2) + 2\underline{C} \rightleftharpoons \underline{Si} + 2CO \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$(SiO_2) + \underline{Fe} = \underline{Si} + (FeO) \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where (x) - slag constituent and $\underline{x}$ - metal constituent.

To decide which way the reactions are likely to go in practice a knowledge of $\gamma_{(SiO_2)}$, $\gamma_{\underline{Si}}$, and $\gamma_{(FeO)}$ is required along with the relevant thermodynamic data. However, $\gamma_{(SiO_2)}$ and $\gamma_{\underline{Si}}$ values are not well established and little attempt has been made to find values for FeO in blast furnace type slags. Arthur(1) investigated the above reactions and decided that reaction (2) was the controlling reaction. While he found that under his experimental conditions Si was in equilibrium with (FeO), in practice this may not be so. Knowledge of γ_{FeO} in blast furnace slags would therefore be of great help in deciding which factors govern silicon distribution in the blast furnace, i.e., whether Si is in equilibrium with (FeO) or with the oxygen potential of the system, carbon-carbonmonoxide if this is different from the oxygen potential of the slag.

A similar situation exists with regard to sulphur distribution in the blast furnace. Knowledge of γ_{FeO} would help in deciding the mechanism of sulphur transfer and whether or not S was at its lowest possible value.

The commonly accepted mechanism for some time has been that iron sulphide partitions between metal and slag and (FeS) then reacts with "excess base" in the slag according to the reactions:

$$[FeS] = (FeS) \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$(FeS) + (CaO) = (FeO) + (CaS) \quad \ldots\ldots\ldots\ldots\ldots(5)$$

Derge, Philbrook and Goldman(2) got experimental support for this view by bringing sulphur-free slag into contact with sulphur-bearing metal in a graphite crucible. Sampling with time showed that the iron content of the slag increased initially along with sulphur content of the slag and thereafter decreased.

For sulphur transfer to proceed by this mechanism (FeO) must be kept below its equilibrium value for reaction (5). This can be done by reduction by the coke floating in the slag or by reaction with carbon of the metal according to the reaction.

$$(FeO) + \underline{C} = CO + \underline{Fe} \quad \ldots\ldots\ldots\ldots\ldots(6)$$

Philbrook and Derge(3) modify this mechanism by suggesting that reaction (5) is unnecessary, i.e., that the four radicals involved are commonly present in the slag phase without any reaction being postulated and for further reaction to proceed ionised oxygen of the slag must be neutralised. The most reducible oxide present is FeO so this means in effect the reduction of (FeO) which they say can be done via reaction (6) or by reduction of FeO by Si or Al.

The mechanism proposed by Ramachandran, King and Grant(4) is that sulphur in the metal must be ionised before being taken up in the slag phase

$$S + 2e = S^{--} \quad \ldots\ldots\ldots\ldots\ldots(7)$$

the necessary electrons being provided by the reactions:

$$C + O^{--} = CO + 2e \quad \text{.....(8)}$$

$$\underline{Si} = Si^{++++} + 4e \quad \text{.....(9)}$$

$$\underline{Al} = Al^{3+} + 3e \quad \text{.....(10)}$$

$$\underline{Fe} = Fe^{2+} + 2e \quad \text{.....(11)}$$

$$\underline{Mn} = Mn^{2+} + 2e \quad \text{.....(12)}$$

Reactions (9), 10) and (12) fit the observation made by many workers that Si, Al and Mn all seem to hasten desulphurisation.

In both of the mechanisms described it would seem that the FeO content of the slag is an important factor in the rate of sulphur transfer and in the equilibrium finally attained.

Taylor and Stobo(5) investigated the mechanism of sulphur transfer and the effect of FeO on it. They found that where carbon crucibles were used, the slag FeO content was not reduced below about 0.1% while their S distribution ratios were in agreement with Hatch and Chipman's(6) results, who got (FeO) values of 0.03% in their slags.

Taylor and Stobo suggest that their FeO values are high because, when the FeO content of their slags drops to the region of 0.1% the reaction :

$$(SiO_2) + \underline{Fe} = \underline{Si} + (FeO) \quad \text{.....13)}$$

proceeds more rapidly when the metal is far from Si saturation than does the reduction of (FeO) by C when FeO content is very low. This explanation depends on the fact that Hatch and Chipman's metal contained silicon at values approaching equilibrium with slag silica while Taylor and Stobo's metal was low in silicon.

From the agreement with sulphur distribution values found by Hatch and Chipman, Taylor and Stobo suggest that sulphur distributions can be obtained corresponding to the C-CO oxygen potential while the FeO content of the slag is higher than corresponds to such an oxygen potential.

This means, according to Taylor and Stobo, that the mechanism cannot be controlled by FeO in the slag and that the reaction must depend on an interfacial reaction which can be expressed:

$$\underline{S} + O^{--} = S^{--} + \underline{O} \qquad (13?)$$

the oxygen of the metal at the interface governing the approach to equilibrium and the equilibrium finally attained.

At relatively high values of FeO in the slag, the slag FeO content could control $\underline{O}$ but at low values it is suggested that reaction (13) keeps the FeO of the slag high while $\underline{O}$ in metal at the interface is reduced to a value approaching the C-CO oxygen potential, this being the oxygen potential that controls sulphur transfer.

These suggestions do not conflict with the conclusions reached by Ramachandran, King and Grant(4) who say that one way of providing electrons for ionisation of sulphur is by discharge of O^{--} by reaction with C at the slag-metal interface.

To decide if blast furnace practice is giving as good sulphur distribution as can be attained it is necessary to know, (1) if equilibrium between slag and metal is attained, and (2) if the slag is at as low an oxygen potential as the oxygen potential of the system carbon-carbon monoxide at the effective pressure of CO in the blast furnace.

Reported values of FeO in blast furnace operation lie between 0.2 and 1.0% FeO. The high end of this range is almost certainly in error due to the difficulty of separating metallic iron from blast furnace slag before analysing for FeO and most probably the lower values reported are higher than the true FeO contents of the slags analysed. (This problem is discussed more fully in the Appendix.)

At the prevailing temperatures and CO pressures in the furnace, a_{FeO} should be about 0.02%. There is a possibility then that the lower FeO values reported do correspond to equilibrium with C-CO. This could be the case if values of γ_{FeO} are very low.

The slags may be at equilibrium even if γ_{FeO} is not low, however, because of the analysis problem mentioned above giving rise to falsely high FeO concentrations.

Evaluation of γ_{FeO} could thus help decide whether or not blast furnace slags are in equilibrium with the gas phase and/or the metal phase.

It was therefore decided that direct investigation of the reaction

$$(FeO) + \underline{C} = \underline{Fe} + CO$$

would be worthwhile, particularly if conditions could be so controlled that γ_{FeO} could be calculated for FeO contents of $<1\%$ by weight in blast furnace type slags.

REVIEW.

REVIEW.

A great deal of work has been done on slag and metal problems associated with the blast furnace. In a great many cases the activity coefficient of iron oxide is of direct interest and in many others the state of oxidation of the slag which is indicated by, among other possibilities, the iron oxide activity of the slag, is important.

Whilst little work has been done on the direct estimation of γ_{FeO} in blast furnace slags a considerable amount has been done on steel-making slags. Most of the steel-making data are concerned with high FeO slags but there are results available on low FeO electric steel-making slags.

Data for ordinary steel-making slags have been reviewed by Bishop, Lander, Grant and Chipman(7) [See Fig.8]. These values are based on values of a_{FeO} calculated, according to Taylor and Chipman(8), from the ratio of the oxygen content of the metal in equilibrium with the given slag to the saturation oxygen content of the same metal which is assumed to be in equilibrium with an a_{FeO} value of 1.0. It is fairly well established that between zero and oxygen saturation the activity of oxygen in the metal is proportional to its concentration. Such values of a_{FeO} may be accurate but use in blast furnace slags involves a long extra-polation to $\sim$1.0% FeO from 10% FeO the lowest concentration given by the authors.

Turkdogan and Pearson(9) also reviewed the available data on slag-metal equilibria. Their results on a_{FeO} are given in Fig.9 where it can be seen that they give a_{FeO} values for FeO concentrations of $\sim$2.0 molar per cent.

They calculated oxygen saturation values for the various experimental temperatures given by the workers whose results they reviewed, by the equation

$$\log [O\%] = -6320/T + 2.734.$$

and from the values given for the actual oxygen content of the metal calculated a_{FeO} by the method outlined above. The lower FeO values shown in Fig.9 are based on data given by Rocca, Grant and Chipman(10) who point out that the degree of accuracy of their oxygen in metal figures is of the same order as the values themselves for their low FeO runs. There must therefore be some doubt as to the accuracy of the value of ~ 5.0 for γ_{FeO} at a $CaO.SiO_2$ ratio of ~ 2 indicated by Fig.9. The only values given at lower basicity ratios - which are more applicable - are at $\sim 10\%$ FeO and indicate γ_{FeO} values of ~ 1.0.

It is difficult to compare the values obtained from steel-making slags with those applicable to blast furnace type slags because of the large variation of γ_{FeO} indicated with change in basicity. Thus in the review made by Bishop et al(7), γ_{FeO} is shown to be dropping steeply with decrease in basicity below $CaO.SiO_2$ ratios of 1.0 [See Fig.8]. These slags do not contain much Al_2O_3 of which there is a fairly large amount in blast furnace slags. It is probable that Al_2O_3 as a first approximation may be considered as additive to SiO_2 in these slags when estimating basicity as Al_2O_3 behaves as a network forming oxide in high silica melts. Thus the probable basicity of iron making slags falls in the region where the results from steel making slags indicate

rapid changes in γ_{FeO} i.e., at basicity ratios less than 1.0.

Schuhmann and Ensio(11) made a direct estimate of γ_{FeO} in iron-silicate slag by equilibrating the slag with a gas mixture of CO and CO_2 and an iron crucible. They calculated a_{FeO} from the free energy data given by Darken and Gurry(12) for the reaction:

$$FeO + CO = Fe_{(\gamma)} + CO_2$$

Since $a_{Fe} = 1$, $a_{FeO} = \frac{1}{K} \frac{pCO_2}{pCO}$

Their results, which show considerable negative deviation from Raoult's Law as FeO content decreases are not of much value with regard to blast furnace operation since the FeO concentrations involved lie between 61-93% FeO and the slag contains only FeO and SiO_2.

Michel and Schuhmann(13) took this work further by investigating the equilibria between iron-silicate slags and $CO-CO_2$ gas mixtures when the slags were silica saturated. Again, however, the FeO concentrations involved are outside the range of interest in blast furnace slags as their slags contained more than 40% FeO.

Direct estimates were made of γ_{FeO} in blast furnace type slags in equilibrium with high carbon iron by Arthur(1) while investigating silicon distribution ratios between blast furnace type slags and metals. The method of calculation was based on the reaction:

$$(FeO) + \underline{C} = \underline{Fe} + CO$$

whence $$a_{FeO} = K \frac{a_{Fe} \cdot pCO}{a_{C}}$$

Since the iron contains carbon, silicon and the effect of Si on γ_C must be estimated according to the semi-empirical methods devised by Chipman(14), and Sherman and Chipman(15), and having thus obtained values for γ_C, γ_{Fe} may be found by a Gibbs-Duhem integration. a_{CO} could be taken as 1 under their experimental conditions. In the course of his work Arthur found that to get down to really low values of FeO (<0.1%) the silicon content of the metal had to be very high (~20%) which makes estimation of γ_C doubtful and has therefore a great effect on the accuracy of a_{FeO} calculated therefrom.

Arthur found that for FeO concentrations between 0.3 and 1.4%, Si contents ranging between 0.2 and 5.0% and C contents between 2 and 4%, γ_{FeO} values calculated from such melts were in reasonable agreement with γ_{FeO} values found using simple Fe-C binary melts. Strong negative deviation from Raoult's Law was indicated, the deviation increasing as FeO content increased. γ_{FeO} varied from 0.13 to 0.08 as FeO concentration rose from 0.3 to 1.4%

These values of γ_{FeO} differ considerably from the values indicated at low FeO contents in steel-making slags where γ_{FeO} values of the order of 1-3 are indicated.

The reason for this great difference could lie partly in the fact that in Arthur's work the slags were very high in Al_2O_3 (up to 40%) and it is therefore difficult to decide at what basicity value in the steel-making slags γ_{FeO} values should be taken as comparable since, as indicated in Figs. 8 and 9, γ_{FeO} is dropping greatly from ~3 as the

basicity ratio of the steelmaking slags falls below 1.0 (7). However, the difference is still very great and may be due to the effect of Al_2O_3 itself rather than simply through the effect of Al_2O_3 on the basicity ratio.

EXPERIMENTAL PROCEDURE.

EXPERIMENTAL PROCEDURE.

Theoretical Basis of Experimental Procedure.

Thermodynamic data for the reaction

$$(FeO) + \underline{C} = \underline{Fe} + CO$$

is well established(16) so that if reliable values of a_C, a_{Fe} and a_{CO} can be estimated an accurate estimate of a_{FeO} can be made if such a reaction is brought to equilibrium.

To keep down problems of slag composition control and to have a reasonable knowledge of a_{Fe} it was decided to bring slag to equilibrium with varying partial pressures of CO and with the Fe and C of steel crucibles used to hold the slag . This, of course, limited experimental temperatures to the order of 1450°C or less as the carbon content was varied between 0.6 and 0.2% C.

Initially it was decided to obtain varying CO partial pressures between 0 and 1 atmos. by using pure CO in a vacuum tight system pumped down to the required pressure. This will be referred to as the "static" method.

It was eventually established that no useful range of FeO content could be covered by this method but that many difficulties could be overcome if the required partial pressure of CO was obtained by mixture with an inert gas and the mixture passed in a continuous stream round the crucible. The gas chosen was Argon. Most of the results were obtained by the use of these Argon mixtures. This method will be called the "dynamic" method.

Steel crucibles were first prepared by carburising Armco iron at 1000°C according to the data given by Smith(17) so that a_C could be obtained for a simple Fe-C binary system. So many crucibles were required, however, for establishing the technique that eventually mild steels with the requisite carbon contents were used for crucible manufacture.

Fig. 1.

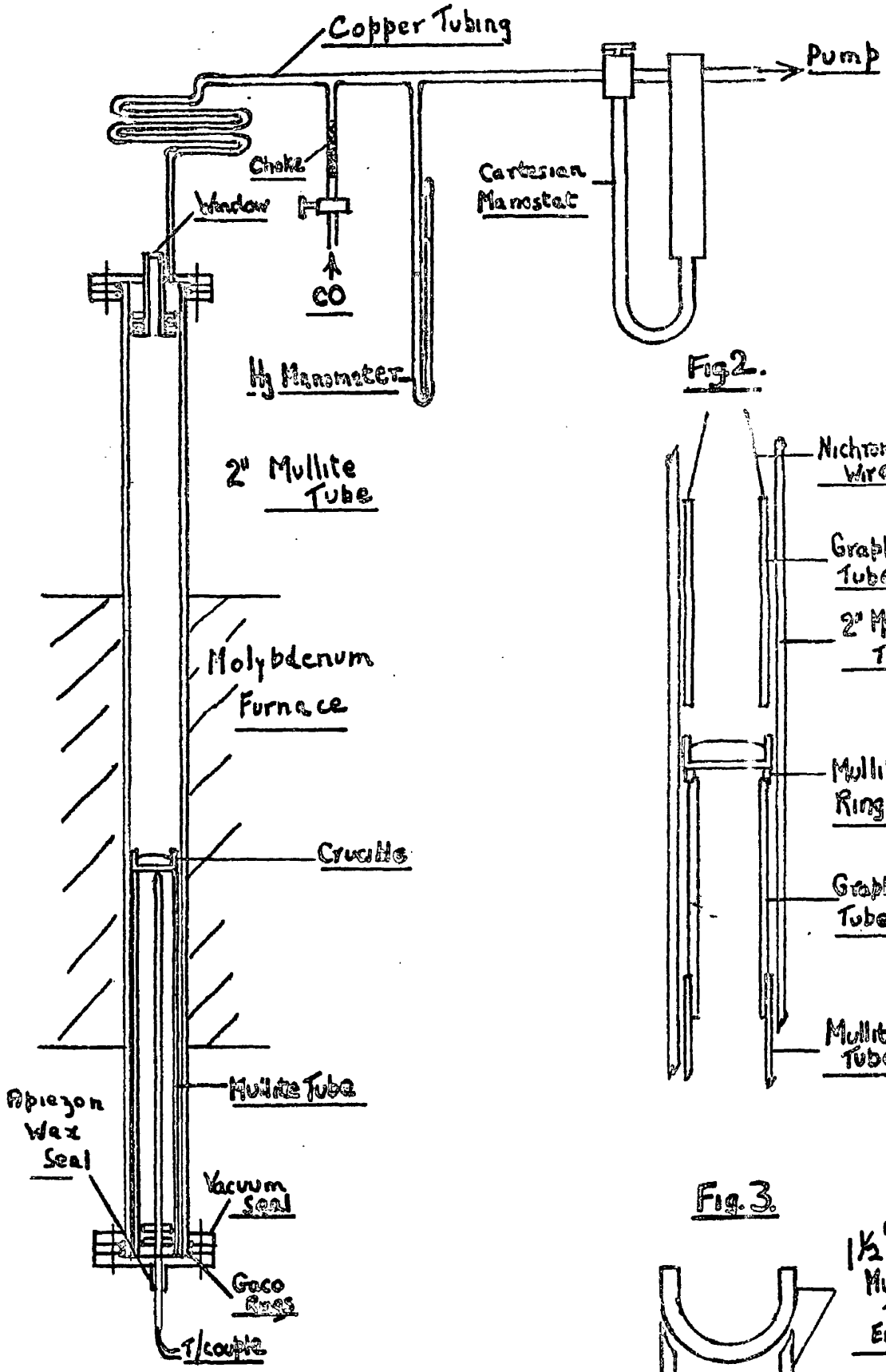


Fig 2.

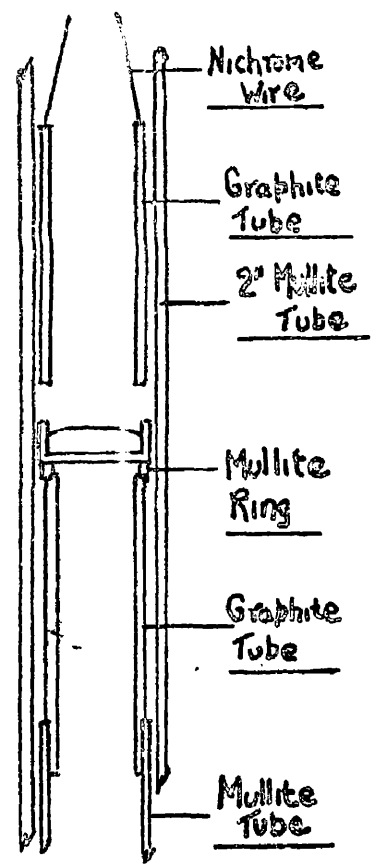
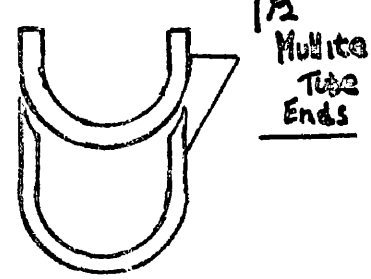


Fig. 3.



Static Experiments.

Apparatus Used.

A diagrammatic representation of the apparatus used is shown in Fig.1.

The Cartesian Manostat controls the "system" side of the instrument to any given pressure as long as that pressure is higher than the pressure maintained on the pump side. For satisfactory operation there should be a "bleed in" to the system side to ensure that the pressure does not fall below that required.

Polyvinyl chloride (P.V.C.) tubing was found to give very satisfactory joints between metal and glass, while metal to metal joins were made either with the use of Gaco sealing rings or by means of simple brass cup and cone seals.

The 2" mullite reaction tube was found to withstand a pressure difference of one atmosphere at 1400°C, but at 1500°C collapsed on heating overnight. The system could be vacuum tested in the cold but gas evolution made vacuum testing impossible at working temperatures. Experience indicated, however, that slight leaks which could not be recognised by increase in gas removal by the pump via the Cartesian Manostat caused oxidation of the steel crucible. If there was no

sign of an oxide skin on the crucible it was assumed that the system was satisfactory.

Crucible dimensions were : o.d. 1.5", depth 0.5" and wall thickness .0625". This shallow pan shape was adopted to give maximum area of contact for the gas-slag interface. The crucibles were machined from Armco iron and then carburised at 1000°C. A high carbon content was wanted to give low FeO values but was limited to $\sim$ 0·4% C because of the experimental temperatures required, i.e., 1400°C+ .

Carburising was done by CO-CO_2 gas mixtures at 1000°C. Data given by Smith(17) indicates that at 1000°C a gas mixture of 94.5% CO, 5.5% CO_2 is in equilibrium with 0.4% C in austenite. As the carbon contents of the crucibles used in the first series of runs show, some difficulty was found in attaining this figure possibly due to carbon deposition from the gas. The vitreous silica tube used as a reaction tube soon showed a large amount of such deposition. This observation is significant in view of the difficulties attributable to carbon deposition found in the later experimental work.

However, by pumping out the system and filling with CO before starting to pass the required gas mixture and by running at 4% CO_2, crucibles containing 0.4% C. were eventually obtained.

Slags were made from CaO, Al_2O_3 and SiO_2 to approximate to blast furnace slag composition. They were melted in graphite crucibles by a high frequency induction unit, cast, crushed, remelted and granulated by casting into water. The granulated material was then crushed, sampled and analysed.

FeO containing slags were made up by adding FeO powder to the crushed $CaO/SiO_2/Al_2O_3$ slags and premelting in an iron crucible in a nitrogen atmosphere. The slag was then analysed for FeO before use.

The slags used were of the following compositions.

	Wt. Percentage.			Mole Basis.		
	CaO	Al_2O_3	SiO_2	CaO	Al_2O_3	SiO_2
Slag A.	45.7	16.8	37.4	.510	.102	.388
" B.	40.0	18.5	41.5	.450	.114	.436
" C.	40.5	22.6	36.9	.464	.142	.394

Preparation of FeO.

The FeO powder used was prepared by heating ferrous oxalate in vacuum to 1000°C and quenching in vacuum after 2 hours at temperature.

Analysis.

The analyses required were for carbon in metal and ferrous oxide in slag.

Carbon was analysed by the normal combustion method.

Analysis for FeO was done by a colorimetric method in which iron in solution was reduced by hydroxylamine hydrochloride and then coloured by addition of orthophenanthroline ~ 1.10 (18). The depth of colour was measured by means of a Hilger Spekker Absorptiometer. By suitable adjustment of sample weight, dilution and cell length a range of 0 to 1.5% FeO was conveniently covered, the range of the method being 0 to 6 p.p.m.

of Fe in a 1 cm. cell.

The separation of metallic iron from slag can be a problem in experimental work of this kind as it is in blast furnace slags. It has been found by many workers (5),(1),(19), however, that metallic iron can be separated quite readily by mechanical or magnetic means except where sulphur is present. This finding was confirmed in the present work where sulphur was absent from slag and metal. Most of the metallic iron reduced from FeO collected on the surface of the slag and could be readily separated by magnet. The magnet was used on first knocking the slag out of the crucible, after crushing and again after grinding for analysis. Results obtained in this way were no different from results got by taking one lump of clear glass and analysing that lump for FeO. The latter method, however, would not have been reliable as normal practice as a slag may have been inhomogeneous or a particle of iron might have been present in a chosen lump.

Experimental Procedure.

In this section of the work, using static conditions, there was a continual search for a suitable technique until finally it was decided that the method would not give the results required. This means that there was a modification required for practically every run and the runs cannot be usefully set out in tabulated form apart from one or two short series. The results will therefore be incorporated in this description of procedure.

From the available data and assuming that γ_{FeO} in these slags was of the order of 1 to 3, it was estimated that with 0.4% C in the metal at 1450°C a CO pressure of 10 gm. Hg would give FeO concentrations at the lower end of the range it was desired to investigate.

Because the Cartesian Manostat operated most satisfactorily when the presence of the system tended to rise above that required and because it seemed likely that the reaction would go more easily from the high FeO side towards the formation of CO it was decided to start the work with excess FeO present. Thus FeO added was about 0.4%. Slag and crucible weights were such (9 gm. and 20 gm. respectively), that even if all the FeO was reduced there would be no significant alteration of C content of the crucible.

The procedure initially decided upon was to heat the furnace to about 900°C with the system under vacuum, then fill with CO, and pump out (repeat once or twice) thus flushing the system out with CO. The system was then pumped down to the pressure required and the furnace taken quickly to the experimental temperature. The furnace was then held at temperature for two hours and cooled. To help keep the system vacuum tight no arrangements were made for sampling during the run or for quenching the crucible and slag.

The first four runs carried out showed that no matter how vacuum tight the system was made virtually all the carbon was lost from the metal crucibles. It was also found that 1450°C was a rather high temperature for the mullite tubes at such a low pressure and all later static runs

were done at 1400°C with slag B which alone had a low enough melting point.

The loss of carbon could be attributed to several possibilities, two of the more likely being:

(a) Silica in the slag could react with C of crucible thus:

$$(SiO_2) + \underline{C} = (SiO) + CO$$

This possibility was checked by heating some slag at 1400°C in a graphite crucible in the furnace at 9 cm.Hg. pressure of CO. Thus the slag could reach an equilibrium amount of SiO and there should be no further attack on the carbon in the steel crucible when used in a run.

Using such a slag in the next run made no difference to the carbon loss so the next possibility was investigated.

(b) If carbon deposition was occurring at any significant rate CO_2 would be formed at cooler parts of the tube probably about 400-500°C. This CO_2 would diffuse to the reaction zone where it would be in excess of the amount at 1400°C in equilibrium with the steel crucible. Reaction with carbon of the crucible

$$C + CO_2 = 2CO$$

could occur and thus by continual production of CO_2 at the cooler parts of the tube with reduction to CO at the hot zone eventually denude the reaction crucible of carbon.

It was quickly found that reaction (a) was not solely responsible for the carbon loss when a run was done without any slag in the crucible, i.e. this crucible again lost all its carbon.

Further investigation using mild steel samples showed that this loss could be prevented by a set up as shown in Fig.2. The graphite tubes above and below the reaction zone were of such a length that they covered the temperature drop between the hot zone and 400°C. Thus any carbon solution reaction following upon carbon deposition could take up carbon from the graphite tube rather than from the crucible. Using this technique runs 10 and 11 gave the following results.

	CO pressure.	$C_{(start)}$	$C_{(final)}$	$FeO_{(start)}$	$FeO_{(final)}$
Run 10.	10 cm. Hg.	.43	.35	.4	.14
Run 11.	10 cm. Hg.	.42	.37	.14	.14

Examination of a micro section of the crucible from run 10 showed some carbon loss from the rim of the crucible. For run 11 the system was degassed at 1400°C before cooling and inserting the crucible and slag. This seemed to give better results. Degassing of graphite is very troublesome(20) and may have led to more trouble if this method had not been abandoned for other reasons.

These results would seem to give an equilibrium figure for FeO in the slag at the C in iron and CO figures quoted. For reasons made clear in the later work, however, the FeO has not come down far enough to reach equilibrium.

Having got these results, however, which seemed satisfactory another series of runs was done to explore the effect of variation of CO pressure so that the desired range of FeO could be covered.

The following results were obtained.

Run	CO pressure.	FeO(start)	FeO(finish)	C(start)	C(finish)
12	3 cm.Hg.	.4	.12	.42	.25
13	" "	.4	.11	.35	.10
16	" "	.4	.11	.39	.13
19	" "	.5	.12	.34	.13
14	24 cm.Hg.	.5	.21	.35	.44
17	" "	.5	.21	.31	.38

These runs show that at low pressures C loss still occurs while runs 14 and 17 were unsatisfactory also, because it was found by examination of micro-sections that the crucible rim above the slag line was heavily carburised. The figures quoted are for C content of crucible metal below the slag line. C content in the rim above the slag line analysed at 0.60% C.

The loss of carbon was undesirable because it was doubtful if the FeO values obtained when the carbon content dropped as low as the values shown, would be in the range required. Also, there was doubt from the appearance of the micro-sections as to what would be the equilibrium carbon content.

It was therefore decided to investigate the loss of carbon at the lower pressure and to find means of stopping the loss.

In one such attempt the slag was again preheated in a graphite crucible at a CO pressure of 3 cm.Hg. to check the possibility of the oxygen potential of the slag being controlled by that of SiO_2/SiO. This had no effect on the carbon loss.

It seemed possible that the process of carbon solution following on carbon deposition in the cooler parts of the furnace was again occurring, i.e., that the graphite tube shields were not effective at the lower pressure.

If this were so then it appeared possible to stop the process by slowing down the rate of diffusion of gas to and from the crucible. This was attempted by placing the crucible in an alundum crucible with a lid but with no success.

A series of runs was then carried out using mild steel samples alone instead of crucibles containing slag. In this series different attempts were made to seal off the metal from the gas in the combustion tube while leaving enough of a leak to keep the gas round the metal at the same pressure as the reaction tube. Many attempts were made to arrive at the best method of attaining this aim. However, even when the crucible was sealed fairly efficiently by grinding the edge of a solid bottom mullite tube to a hemispherical seal-to match the hemispherical bottom of another tube used as a lid - as in Fig.3, it was still found impossible to stop the loss of carbon from the metal.

In all these runs it was found that the lower the pressure of the system the greater or more rapid was the loss of carbon. When the metal was thus enclosed there was always a deposit found on the under side of the lid of the mullite container, and it seemed possible that

this deposit was due to loss of carbon possibly as an iron carbon or an iron carbon oxygen compound. If this were so then the vapour pressure of the volatising substance should have been measurable.

It was decided to investigate this possibility by arranging a steel specimen in a furnace so that there was a flow of argon past the specimen. By decreasing the rate of flow of Argon and by measuring the loss of weight from the specimen an estimate of the vapour pressure of the volatilising substance could be made. Also the loss of weight taken in conjunction with the change in carbon content would give an indication of the form in which the carbon was being given off.

The furnace used was platinum wound with a 1" mullite reaction tube. The reaction zone in which the steel specimen was suspended by Pt.wire was enclosed by alundum pieces so that the Argon gas was released just below the specimen and collected just above it so cutting down possible diffusion of gases to and from dead spaces in the reaction tube.

After many runs it was found that if the Argon was pure enough and if the system was made gas tight there was no loss of carbon from the steel although there was a measurable loss of weight due to iron volatilisation.

This rules out loss of carbon as a carbide in the absence of CO. The question of whether an iron carbon oxygen compound can be formed is more difficult as, in the presence of CO carbon is picked up by carburisation. This makes it very difficult to check on evaporation losses in view of the small weight changes involved.

If an iron carbon oxygen compound was formed an increased loss of iron could be expected but there was no evidence that this occurred.

In the light of this work the effects found in the static experiments could be summarised as follows.

At low pressures ($\sim$ 3 cm.Hg.) carbon was lost from the crucible either through carbon deposition in the cool zones in spite of the graphite shields or by volatilisation involving carbonyl formation.

At high pressures of CO ($\sim$ 26 cm. Hg.) carbon may be taken up by the steel by the following mechanism. The graphite shields extended into the reaction zone next to the crucible. There is then a carbon activity near the crucible which is very much higher than the carbon activity of the steel crucible itself. Thus the small amount of CO_2 in equilibrium with CO and carbon of the steel crucible is in excess of that in equilibrium with the graphite. Thus CO_2 is at a lower concentration next to the graphite shield and diffusion of the gases could lead to CO_2 reduction at the graphite and CO_2 formation with deposition of carbon according to the reaction.

$$2CO = \underline{C} + CO_2$$

at the steel crucible surface. However, why variation of working pressure should reverse the direction of carbon transfer is difficult to explain.

The deposit which was found on the refractory crucible lids used in the experiments wherein attempts were made to cut down the diffusion of carbon from the steel crucible by sealing off the metal from the reaction chamber, is most likely to be iron. There was also found to be a measurable loss of weight in the vapour pressure experiments even when

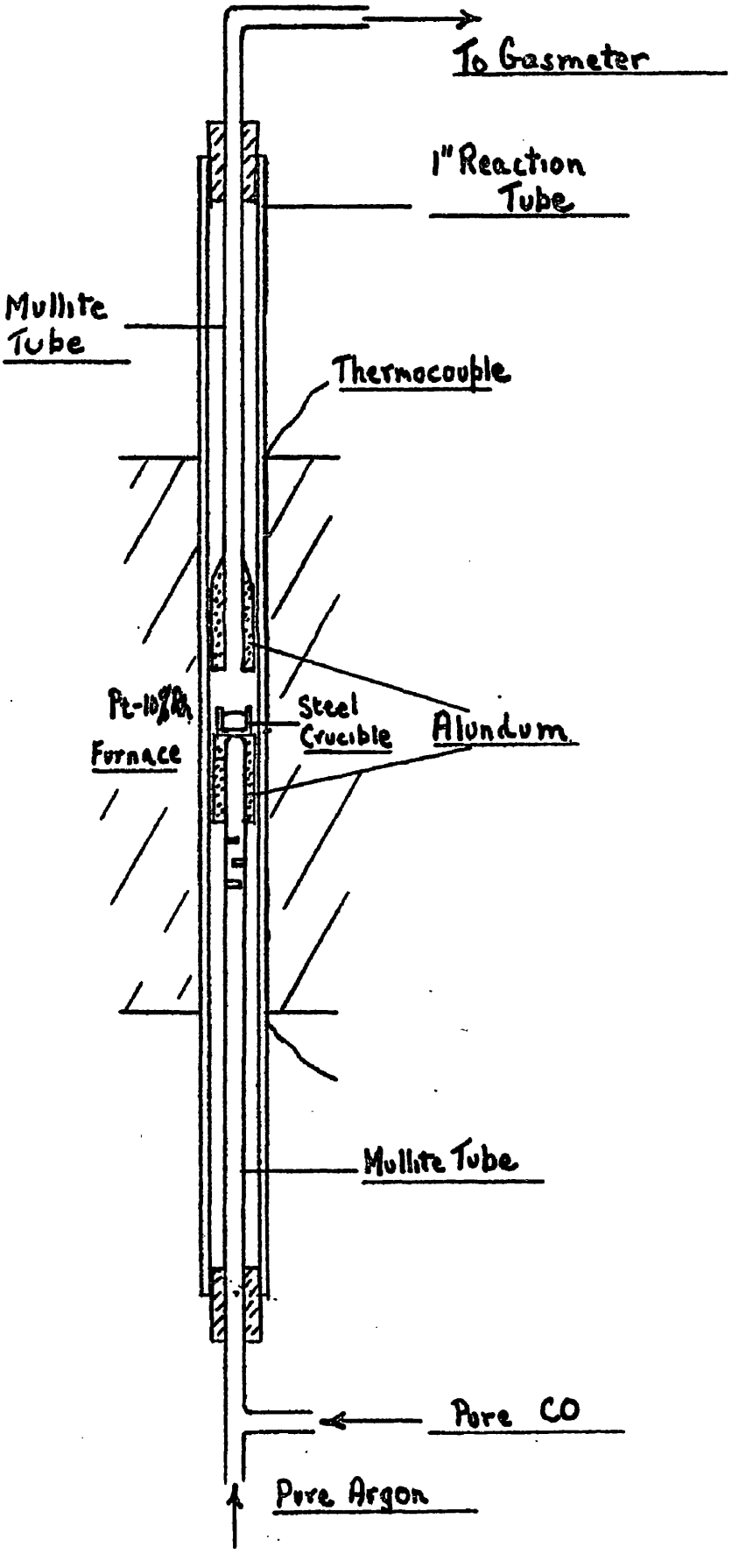
no loss of carbon was observed. This was also attributed to iron volatilisation. This volatisation of iron means, of course, that a catalytic agent is quickly deposited in the carbon deposition zone of the reaction system and makes the carbon deposition problem very intractable.

It was established therefore that carbon deposition and difficulties would make it very difficult to keep the various constituents at the concentrations desired, for example there would not be pure CO in the system. However, this would not be significant as at 1400°C the CO partial pressure could be taken as the pressure of the system with no significant error arising.

But the effect on carbon content of the metal is so drastic that it was decided to abandon the method and establish the required partial pressure of CO by mixing with Argon. If such a gas mixture is then passed in a stream round the crucible containing the slag, it should prevent loss of carbon by carbon deposition. Since there will be no graphite shields required then the possibility of carbon pick-up should not arise.

Accordingly the method described in the next section of the work was developed.

Fig. 4


To Gasmeter
1" Reaction Tube
Mullite Tube
Thermocouple
Pt-10% Rh
Furnace
Steel Crucible
Alundum
Mullite Tube
Pure CO
Pure Argon

Dynamic Experiments.

Apparatus.

The equipment used for this work is shown diagrammatically in Fig.4.

The furnace was wound with 20 gauge Pt/10% Rh. wire and designed to take a 1" mullite tube.

Purified Argon and carbon monoxide both from cylinders, were mixed just before entering the bottom of the furnace and the gases were taken off just above the crucible, passed out of the top of the furnace and through a gas meter which measured the total flow of gases. The CO inlet was metered by means of a flowmeter with a water column blow-off so that the gas mixture could be adjusted to the composition required by setting the CO flow and adjusting total flow by variation of Argon input. This composition was checked by analysis in a Bone and Wheeler apparatus.

Considerable difficulty was experienced in making the apparatus gas tight. At first it was thought that this would not be critical as the gas was flowing at a few inches of water pressure above atmosphere. It was discovered however that very slight leaks were enough to allow air to diffuse against the stream of gases escaping via the leaks.

There were two chief sources of leaks. One was in the purifying train set up for the Argon. This train consisted of a tube of soda asbestos to remove CO_2, a tube of magnesium perchlorate to remove moisture and then the gas was passed over a tray of phosphorus pentoxide

which was used more as an indication that the gas was thoroughly dried. The gas was then passed through tubes of calcium metal turnings heated to 650°C to remove any traces of oxygen.

It was found necessary to make all this part of the train of metal, i.e., brass containers with rubber seals for the drying and CO_2 removal and 18/8 stainless steel for the calcium containing tubes. Copper tubing was used to connect the various portions of the train.

The second and most difficult problem was that of the reaction tube. A tube could show as being perfectly vacuum tight at room temperature but would open up at working temperature. Such a tube would often appear vacuum tight when tested at room temperagure again. It was assumed that the normal impermeable mullite tubes would be suitable for the temperatures required but satisfactory results were only obtained when recrystallised alumina tubes were used. Even with such tubes one tube in three was unsatisfactory, another would only give half a dozen runs and the third upwards of 20 runs.

The CO was also dried and cleaned of CO_2 but this part of the train gave little trouble.

Analysis of the gas mixtures was done by putting a sampling tube into the circuit at the outlet end of the furnace and taking a sample over at least 2 hours. Such samples showed no measurable CO_2 or O_2.

Gas flow rates were of the order of .005 to .01 $ft.^3/min.$ with CO contents ranging from 5% to 50%.

The crucibles used were 0.5" in diameter, about 0.5" deep and had a wall thickness of .0625". They were made of mild steels containing .1 to .4% C.

The slags used were those given in the static method. Slag B was suitable for temperatures from 1400°C up but slags A and C were too high melting to be used below 1450°C. It was found desirable to premelt the slags to get the required iron oxide content rather than to mix FeO powder with crushed slag for any given run.

The weights of slag and crucible were 2 and 10 gm. respectively.

Experimental Procedure.

The procedure first used was to insert crucible and slag, pump out the system, fill with Argon and heat the furnace to 1200°C. The required flow of CO/Argon mixture was then started. The furnace was then taken rapidly to reaction temperature. It was hoped thus to avoid excessive carbon pick up by the crucible at low temperatures. The CO was cut off on reaching 1200°C on cooling after 2 hours at temperature.

The first dozen runs gave no useful results but established several facts of significance to the technique required. The results obtained were of little use because the lower end of the FeO concentration range was aimed at mostly and for reasons discussed later, such values are unobtainable under the conditions used in this work.

The following factors relevant to technique were found to be significant:

(a) Since the premelted slags are glassy, reaction may start below 1200°C or at least below the temperature at which the CO

concentration required is attained, so that very low partial pressures of CO, operative on heating and cooling, may reduce the FeO concentration below that which should hold for the CO composition assumed to be operative.

(b) The reaction will only go one way with any reasonable speed, i.e., equilibrium must be approached from the high FeO side with evolution of carbon monoxide. Even a six hour run produced no increase in FeO when equilibrium was approached from the low FeO side.

(c) With higher CO compositions the gas carburises the crucible.

Points (a) and (b) showed that the technique could be modified satisfactorily by putting the gas mixture on early. At lower temperatures a given CO concentration should give a higher FeO than at higher temperatures but point (b) shows that the reaction will not go that way. Further, the system can be cooled in the experimental gas mixture without the FeO moving from the value established at working temperature.

However, since the reaction only goes one way it meant that equilibrium was difficult to establish. To do so two approaches were possible. One was to start from different levels of FeO and for different lengths of time for various runs and so establish equilibrium values. This was unsatisfactory because the reaction slows up considerably as it approaches equilibrium and also because for many of the runs point (c) is important, i.e., the crucible is carburising and so C content increases with time and the equilibrium value of FeO is thus diminishing.

These facts make it difficult to assess the meaning of runs carried out in the fashion suggested.

The other approach was to aim at a certain value of FeO by using a CO composition and C content thought suitable and use a set time for each run. The slag is then analysed after the run and the run repeated using the same slag till a constant value of FeO is attained. This means that a minimum of 3 and sometimes 5 or 6 runs are required to establish one point but although laborious, this method does give a true equilibrium value for FeO.

The technique thus established consisted of the following routine.

The crucible with its charge of slag was put into the furnace and the system pumped out and tested for leaks. The system was filled with Argon and Argon flow and carbon monoxide flow adjusted to the composition required. The furnace was then switched on and brought to temperature. Normally the working temperature was held for four hours. After the furnace was switched off, the gas flow was continued till the furnace cooled to 900°C. At this temperature the carbon monoxide flow was stopped and the furnace cooled overnight with a trickle of Argon passing over the specimen.

After analysing the slag for FeO and the crucible for C, the same slag was charged in a new crucible and the run repeated. This was done until a constant FeO value was reached.

Half of the results were got by use of 0.4% C crucible and others by using 0.1% carbon crucible, with varying CO contents in the gas.

At 50% CO these carburised to 0.6 and 0.3% C respectively on a 4 hour run. The results obtained at the higher end of the FeO range (0.8 - 1.0% FeO) required a modification to the technique described above. For these runs it was found that the finishing carbon content was too high for the CO content of the gas which could be used ($\sim$ 50% CO). Reducing the time of the run or the starting carbon content of the crucible had little effect on the final C figure reached. Increase of CO content would probably have meant more rapid carburising. To get to the higher FeO values then at 50% CO in the gas meant keeping the carbon content of the crucible to about 0.2%.

This was done by heating the system in Argon to 900°C and then starting the CO flow holding for 2 hours at temperature and cooling as described above. This gave satisfactory results. It seemed most of the carburising was occurring on heating and the slag was not reacting before the desired gas composition was reached. This was shown by runs DI, DJ and DK, Table 5, where it can be seen that in a slag containing FeO below the equilibrium amount will not lose or gain FeO but above the equilibrium amount will lose FeO until the equilibrium figure is reached, if necessary by a succession of runs. This technique was necessary for runs done at 1450°C and at 55% CO to give carbon in the crucible a finishing value of $\sim$ .18% C.

In the runs using these two techniques the crucibles were examined for distribution of carbon in the crucible walls. In no case was there any indication of a carbon concentration gradient from one side of the wall to the other.

Nor was there any sign of carbon build up in the walls of the crucibles above the slag line as had been found in the "static" work. This observation held even in those runs where the carbon concentration increased markedly, i.e., using a gas composition of 55% CO.

Higher FeO concentrations than those quoted could not be reached by the technique described because of the carburising effect of high CO gas mixtures. To increase the range of FeO covered would have required the use of CO CO_2 gas mixtures utilising the reaction :

$$Fe + CO_2 = FeO + CO$$

As has been shown, however, such a method would give rise to great errors due to carbon deposition problems as discussed on page 48.

RESULTS.

RESULTS.

The results are tabulated in Tables 1 to 5. Each series represents an attempt to reach equilibrium FeO content for a given CO pressure in the system and C content in the steel crucible.

These series in which it has been judged that equilibrium was attained are marked by asterisks.

Where equilibrium was not reached it was due to the very slow rate of reaction at low values of FeO. This held for ovens where a value less than 0.12 to 0.13% FeO was to be expected. This is illustrated by Series 17, 18 and 19, in Table 1; Series 20 and 21, in Table 2; and Series 22, 23 and 24, in Table 3.

In run BP in Series 24, and runs BL and CB, Series 19, pure Argon was used so that the partial pressure of CO was virtually zero and all FeO should have been reduced. Yet the FeO content did not drop from 0.11%.

In run BR, Series 24, the carbon activity was raised to 1 by using a graphite crucible and pure Argon was passed through the system. Even under these conditions the FeO was only reduced to 0.07% from 0.11% after 4 hours.

In most cases it was obvious when equilibrium had not been reached because of this sluggishness. This could be seen by comparing the FeO value obtained for a given CO pressure and crucible carbon content with the result obtained in a series where conditions were less reducing and a consistent δ_{FeO} value had been obtained. This point is discussed more fully in the discussion of results.

Where both C and CO values had altered in such a way as to make it difficult to assess whether or not equilibrium had been attained, calculation of γ_{FeO} decided the issue since γ_{FeO} is found to be decreasing with FeO concentration and a falsely high FeO concentration for a run gives rise to an inconsistently low γ_{FeO} value.

This is shown by the estimation of γ_{FeO} for run BG, Series 22, compared with Series 12 in Table 3.

In Table 5 is given a series of runs which support the assumption that the reaction will only go towards CO evolution and FeO reduction under the experimental conditions used in this work.

In all cases where iron oxide was reduced to iron, the iron appeared as a thin scum on the surface of the slag. This fact was also reported by Philbrook and Kirkbride(19), who investigated the rate of reduction of FeO from slags by carbon saturated iron in graphite crucibles. They found that the reduced iron gathered in beads to form a ring round the slag surface adjacent to the crucible wall. In the present work there was no sign of the iron concentrating at the rim in this fashion.

TABLE 1 - Slag B 1400°C.

	Run No.	Duration (hours)	Final C (%)	FeO(%) Initial	FeO(%) Final	N_{FeO} Final	γ_{FeO}
Series 1	CO-55%. Initial Crucible Carbon 0.10%.						
*	CX	4	.265	2.0	1.32		
	CZ	4	.25	1.32	1.0		
	DP	4	.23	1.0	.86	.0076	1.06
Series 2	CO-27.5%. Initial Crucible Carbon 0.10%.						
*	DE	4	.15	1.0	.73		
	DG	4	.14	.73	.72	.0063	1.05
Series 3	CO-55.0%. Initial Crucible Carbon 0.40%.						
*	AI	4	.55	.5	.36		
	AK	2	.53	.6	.53		
	AS	6	.59	.74	.41		
	AV	6	.55	.6	.45		
	DL	4	.51	.44	.23		
	DS	4	.54	.23	.23	.0020	1.36
Series 4	CO-27.5%. Initial Crucible Carbon 0.40%.						
*	N	2	.40	.36	.24		
	AG	4	.45	.36	.24		
	AX	4	.45	.60	.49		
	AJ	4	.44	.36	.21		
	AL	4	.47	.53	.30		
	DR	4	.40	.17	.15	.0013	1.46

TABLE 1 - Slag B 1400°C (Cont'd).

Run No.	Duration (hours)	Final C (%)	FeO(%) Initial	FeO(%) Final	N_{FeO} Final	γ_{FeO}
Series 17	**CO-13.1%. Initial Crucible Carbon 0.40%.**					
E	2	.40	.21	.15		
L	2	.37	.12	.12		
BK	5	.40	.18	.15		
Series 18	**CO-5.1%. Initial Crucible Carbon 0.40%.**					
BA	4	.41	.18	.13		
BC	4	.41	.13	.115		
BE	4	.40	.115	.115		
BO	4	.40	.11	.12		
Series 19	**Pure Argon Initial Crucible Carbon 0.40%.**					
BL	4	.41	.11	.11		
CB	4	.40	.12	.12		

TABLE 2 - Slag B 1450°C.

	Run No.	Duration (hours)	Final C (%)	FeO(%) Initial	FeO(%) Final	N_{FeO} Final	γ_{FeO}
Series 5	CO-55%. Initial Crucible Carbon 0.10%.						
*	DD	2	.175	2.0	1.41		
	DF	2	.18	1.41	1.25		
	DH	2	.18	1.25	1.20	.0111	.77
Series 6	CO-55%. Initial Crucible Carbon 0.10%.						
*	CD	4	.32	.74	.63		
	CI	4	.31	.63	.54		
	CL	4	.31	.54	.51	.0044	.90
Series 7	CO-27.5%. Initial Crucible Carbon 0.1%.						
*	CO	4	.195	.51	.41		
	CR	4	.195	.41	.41	.0036	1.02
Series 8	CO-55%. Initial Crucible Carbon 0.40%.						
*	AT	6	.55	.74	.26		
	AV	6	.56	.60	.20		
	CT	4	.56	.20	.18	.0016	1.37
Series 20	CO-13.1%. Initial Crucible Carbon 0.40%.						
	BN	4	.40	.18	.17		
	BQ	4	.40	.17	.15		
	BS	4	.40	.15	.15		
Series 21	CO-5.2%. Initial Crucible Carbon 0.40%.						
	BI	4	.39	.11	.11		

TABLE 3 - Slag A 1450°C

	Run No.	Duration (hours)	Final C (%)	FeO(%) Initial	FeO(%) Final	N_{FeO} Final	γ_{FeO}
Series 9 *	CO-55%. Initial Crucible Carbon 0.10%.						
	DI	2	.18	.9	.81		
	DK	3	.18	.81	.81		
	DN	3	.18	1.00	.94		
	DJ	3	.18	.94	.94	.0081	1.05
Series 10 *	CO-55%. Initial Crucible Carbon 0.1%.						
	BT	4	.32	.70	.58		
	BW	4	.30	.58	.46		
	BY	4	.31	.46	.45	.0039	1.13
Series 11 *	CO-27.5%. Initial Crucible Carbon 0.10%.						
	BV	4	.19	.70	.56		
	BX	4	.19	.56	.45		
	CK	4	.19	.45	.36		
	CM	4	.19	.36	.36	.0032	1.18
Series 12 *	CO-55%. Initial Crucible Carbon 0.40%.						
	AQ	6	.55	.7	.17		
	AY	6	.58	.4	.15		
	BB	2	.58	.15	.14	.0013	1.51
Series 22	CO-27.5%. Initial Crucible Carbon 0.40%.						
	AO	6	.43	.4	.15		
	AW	6	.43	.4	.15		
	BO	4	.42	.23	.15		
	BG	4	.43	.17	.11	.0010	1.40

TABLE 3 - Slag A 1450°C. (Cont'd.)

Run No.	Duration (hours)	Final C (%)	FeO(%) Initial	FeO(%) Final	N_{FeO} Final	γ_{FeO}
Series 23	CO-13.3%. Initial Crucible Carbon 0.40%.					
AX	6	.4	.4	.12		
AZ	6	.39	.2	.11		
BD	4	.40	.16	.11		
BF	4	.41	.11	.11		
Series 24	Pure Argon					
BP	4	.40	.11	.11		
BR	4	Pure Graphite Crucible	.11	.07		

TABLE 4 - Slag C 1450°C.

	Run No.	Duration (hours)	Final C (%)	FeO(%) Initial	FeO(%) Final	N_{FeO} Final	γ_{FeO}
Series 13	CO-55%. Initial Crucible Carbon 0.10%.						
	DJ	2	.18	.70	.70		
	DM	3	.18	1.44	1.16		
	DO	3	.17	1.16	.93		
	DQ	3	.18	.93	.91	.0079	1.06
Series 14	CO-55%. Initial Crucible Carbon 0.10%.						
	CA	4	.34	.70	.54		
	CC	4	.31	.54	.45		
	CG	4	.31	.45	.45	.0040	1.08
Series 15	CO-27.50%. Initial Crucible Carbon 0.10%.						
	CH	4	.19	.45	.34		
	CN	4	.19	.34	.34	.0030	1.22
Series 16	CO-55.0%. Initial Crucible Carbon 0.40%.						
	AR	6	.57	.7	.19		
	CS	6	.57	.19	.13		
	CW	6	.60	.13	.13	.0012	1.62

TABLE 5.

Experiments illustrating the irreversibility of the reaction FeO + C ⇌ Fe + CO under the experimental conditions.

Run	Slag used	CO %	C content of crucible	(FeO) Initial	(FeO) Final	FeO Equilm.
DI	A	55	.18	.9	.81	.94
DJ	C	55	.18	.7	.7	.91
DK	A	55	.18	.81	.81	.94
AE	B	55	.43	.20	.16	.23
AF	B	55	.43	.20	.15	>.23
Y	B	55	.35	.13	.13	>.23
R	B	27.5	.4	.12	.12	.15
S	B	27.5	.4	.11	.11	.15

CALCULATION OF γ_{FeO}.

CALCULATION OF γ_{FeO}.

To calculate γ_{FeO}, a value for a_{FeO} must be obtained from the available data in the literature. The first requirement is the free energy data for the reaction

$$(FeO) + \underline{C} = \underline{Fe} + CO$$

This was obtained from the data given in Basic Open Hearth Steelmaking(6) in the following form.

$$C\ gr. + FeO_{liq.} = CO + Fe_{liq.}$$

$$\Delta G = 28730 - 32.14\ T.$$

Richardson and Jeffes(21) give the free energy change for the reaction

$$Fe_{liq.} = Fe_{solid}$$

$$\text{as } \Delta G = 3,650 + 1.98\ T.$$

So that the free energy change for the reaction

$$C\ gr. + FeO_{liq.} = CO + Fe_{solid}.$$

$$\text{is } \Delta G = 25,080 - 30.16\ T.$$

The standard states of the reactants are;

C - pure graphite, Fe - pure solid iron, FeO - pure liquid FeO.

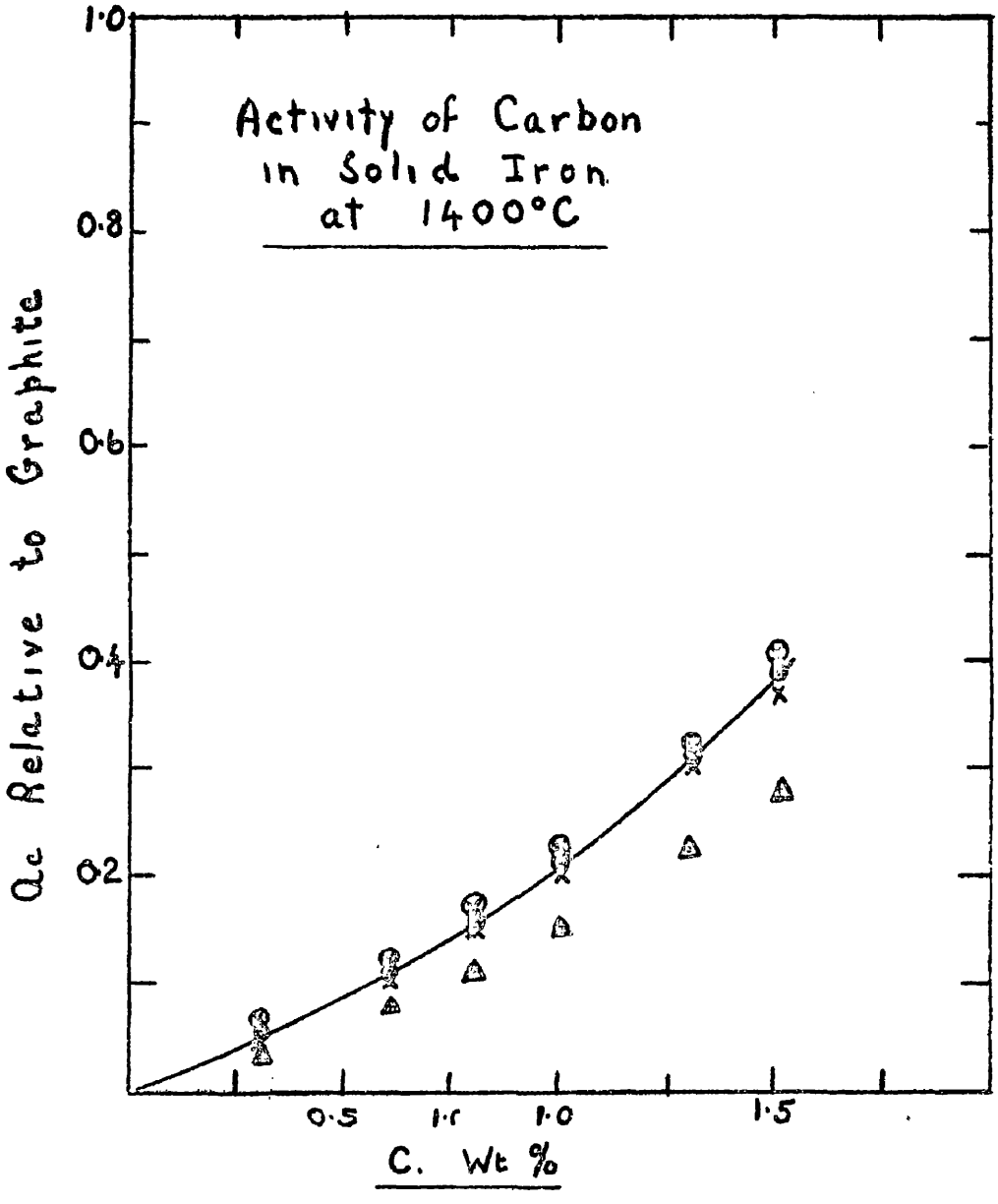
CO - CO gas at 1 atmosphere pressure.

K at 1400°C is 2070 and K at 1450°C is 2576

$$\text{where } k = \frac{p_{CO}.a_{Fe}}{a_{C}.a_{FeO}}$$

γ_{FeO} can therefore be calculated if values can be found for a_{Fe}, a_C p_{CO}.

Fig. 5.



⊗ ⊗ Using $K(P_{CH_4}/P^2_{H_2})$ from thermodynamic data
⊙ ⊙ " " " Smith's "
× " $K(P_{CO}/P_{CO_2})$ " " "
△ " " " thermodynamic "

Activity of Carbon.

Smith's(17) results give values for a_c in austenite at 1000°C and 800°C derived from the carbon contents of steels in equilibrium with gas mixtures of CO/CO_2 and H_2/CH_4. Since the enthalpy change in the reactions involved is very small over the required range of temperature, these reactions can be extrapolated to 1400°C and 1450°C.

Values of a_c against carbon content at 1400°C are given in Fig.5. There is a slight discrepancy between the results for the H_2/CH_4 gas mixtures and those for CO/CO_2 mixtures.

Smith points out that there is a difference between the equilibrium constant ($K = p^2_{CO}/p_{CO_2}$) he obtains experimentally and that given in the literature as obtained from spectroscopic and calorimetric data. Using such data (i.e., K = 166 instead of Smith's value of 137) the corrected curve for CO/CO_2 mixtures is obtained as shown in Fig.5. The discrepancy between the curves for the two different gas mixtures is thereby inc reased.

There is little change in the curve for H_2/CH_4 gas mixtures when independant values of K ($= pCH_4/p^2_{H_2}$) are used instead of Smith's experimental values.

It may be that errors associated with carbon deposition troubles cause the difference between the corrected curve for CO/CO_2 mixtures and the other three curves which can be seen to lie close together. These errors could be cancelled out in the case of the uncorrected CO/CO_2 curve in which Smith's experimentally obtained value for K for the CO/CO_2 gas mixtures is used.

To check Smith's results Chipman's curve given in Basic Open Hearth Steelmaking(20) was used. On investigation it was found that this curve was based on Darken's(22) values, said to be confirmed by Marshall and Chipman's(23) experimental results. The confirmation is very poor and possible reasons for this are given in the discussion of results.

This curve gives values for log f_c on the dilute solution scale. For comparison with Smith's data a_c in liquid has to be found on the ideal scale at a value corresponding to the carbon content of the liquids composition at 1400°C. This value can then be compared with the Smith's value for C in solid iron at the carbon content of the solidus composition at 1400°C.

To convert a_c on the dilute solution scale to a_c on the ideal scale, f_c can be found from Chipman's(20) curve for carbon in liquid iron at a carbon content equal to the carbon saturation composition at 1400°C.

The limit of solubility of carbon at 1400°C = 4.93% C.

log f_c from Chipman's curve at 4.93% C = .772

$\therefore$ a_c in dilute solution scale = 28.9

when a_c on ideal scale = 1

At 1400°C the liquidus composition contains 1.57% C.

From Chipman's curve log f_c for 1.57% C = .178

$\therefore$ a_c on dilute solution scale = 2.34

$\therefore$ a_c on ideal scale = $\frac{2.37}{28.9}$

= 0.082

The solidus composition contains 0.7% C. From Smith's data a_c for 0.7% carbon in solid iron is 0.13. There is, then, poor agreement between the two sets of data.

Darken's values have been reestimated and a revised curve given by Darken and Gurry(24). This is based to some extent on Smith's work and does not give a purely independent check. Treatment as above shows better agreement with Smith, a value of $a_c = .166$ being estimated to compare with Smith's value of 0.13.

Richardson and Dennis(25) give values for a_c in liquid iron but their work only goes up to 1.0 wt.% of C and so cannot be used as a check.

It was decided to use Smith's data extrapolated to give the curve drawn in Fig.5.

The curve obtained for 1450°C was virtually indistinguishable from that given for 1400°C.

The steels used in the present work contained 0.5% Mn, 0.045% S and P, and 0.06% Si. The amount of impurities present is not enough to have any appreciable effect on the activity of carbon.

Iron Activity.

Available data shows that the activity of iron up to 0.6% C is greater than 0.98. Since experimental temperatures and compositions are so near the solidus of the Fe-C system, a_{Fe} was taken as 1.0 as a 2% error in a_{Fe} is well within the range of experimental error.

CO Activity.

CO Activity.

a_{CO} was taken to be equal to the partial pressure of CO in the gas mixture on the assumption that it behaves as an ideal gas.

Given these activities and relevant values of the reaction constant, a_{FeO} can be calculated.

N_{FeO} was calculated on the basis of Moles of the four oxides present, FeO, SiO_2, Al_2O_3 and CaO, and γ_{FeO} obtained from the relationship $\gamma_{FeO} = \frac{a_{FeO}}{N_{FeO}}$.

DISCUSSION OF RESULTS.

DISCUSSION OF RESULTS.

Static Conditions.

The results of the static experiments illustrate the difficulties of using CO and CO_2 gases in equilibrium studies at elevated temperatures. The trouble is that at high concentrations of CO relative to the equilibrium value with C and CO_2 the CO is likely to dissociate and produce C and CO_2.

This was recognised by Schuhmann and Ensio(11) and Marshall and Chipman(23) and in their work both sets of workers took steps to get round the difficulty.

In the present work the presence of CO_2 in small amounts is of no great significance in itself as only the partial pressure of CO is relevant, CO_2 simply acting as a slight diluent. Under static conditions however, it was found that carbon deposition and solution reactions could interfere seriously with the carbon content of the crucible material and make it impossible to establish an equilibrium carbon content in any given run.

Because of this the dynamic experimental technique was adopted wherein the formation of CO_2 was found to be negligible since no C was lost from the crucibles at lower CO values although carburisation took place at higher CO values.

Where gas mixtures of CO and CO_2 are being used to give a certain oxygen potential in the gas phase, conditions are likely to be more difficult to control or interpret than in the present work using only the partial pressure of CO to control the oxidising power of the gas.

It is not easy to ensure that the gas composition shown in the former case by analysis is the effective composition of the gas in the reaction zone. This problem is greater with static conditions as high CO_2 values in the cooler parts of the furnace can be present along with lower values in the reaction zone, through carbon deposition and formation of CO_2 in the colder parts of the reaction chamber.

In Marshall and Chipman's(23) work static conditions were used after they found that their dynamic conditions did not give equilibrium values of CO and CO_2 . They attributed this to dissociation of CO. However, there is little reason to suppose that the samples drawn under static conditions correspond to the effective gas composition in contact with the melt. The gas as analysed would contain more CO_2 than the gas in contact with the metal and lead to low values for carbon activity. There is support for this argument in the fact that their experimental values for γ_C are lower than the calculated values obtained by Darken(22).

Schuhmann and Ensio(11), using flow conditions, checked the gas composition before entering the reaction chamber and after it was bubbled through the melt and found that at gas compositions containing less than 12% CO_2, there was a significant increase in CO_2. This effect is greater at low CO_2 values because the gas is further from equilibrium and, of course, the error introduced is proportionately greater at these lower values.

As shown in the discussion on carbon activities (page 43) there is reason to doubt the accuracy of some of Smith's(17) data and low carbon activities may have been estimated because of carbon deposition in the reaction chamber.

Since the degree of error introduced in this way is an involved kinetics problem under flow conditions the only check on conditions is by careful analysis of incoming and outgoing gas mixtures and even then there is doubt as to the extent to which the gas composition as analysed corresponds to the effective gas composition in the reaction zone.

There must therefore be some degree of doubt attached to the data obtained by Richardson and Dennis(25). These workers used CO/CO_2 gas mixtures flowing past a bead of molten iron. The gas mixtures used were very low in CO_2 and so likely to have significant differences in effective CO_2 compositions from those assumed from the inlet gas composition.

A puzzling feature of the experiments under static conditions was the reversal of transfer of carbon to and from the crucible with change of pressure after the graphite shield was introduced. If the only mechanism for the transfer of carbon is via the $C-CO-CO_2$ reaction there should be a CO_2 concentration gradient between crucible and shield and therefore a tendency for carbon to migrate from the shield to the crucible. As already discussed it was expected that under the experimental conditions the rate of transfer would be slow; in fact at high pressures ($\sim$ 27 mm. Hg.) it appears to be quite fast.

The effect of pressure on the rate of diffusion of CO_2 and hence the transfer of carbon can be derived as follows. The concentration of CO_2 is governed by the reaction:

$$2CO = C + CO_2$$

so that

$$pCO_2 \propto \frac{p^2 CO}{a_c}$$

for $a_c = 1$ and $pCO = 1$; $pCO_2 \propto 1$ at the graphite shield.

for $a_c = 0.1$ and $pCO = 1$; $pCO_2 \propto 0.1$ at the crucible.

If the pressure is doubled then

for $a_c = 1$ and $pCO = 2$; $pCO_2 \propto 4$

and $a_c = 0.1$ and $pCO = 2$; $pCO_2 \propto 40$

Thus doubling the pressure should quadruple the concentration gradient of CO_2 between crucible and shield. The diffusion coefficient of CO_2 will be halved by doubling the pressure so that there will be an increase in rate of carbon transfer from shield to crucible with increase in pressure.

However, this analysis only shows that the rate of transfer of carbon could be altered and not that it would be expected to reverse its direction.

A change of rate of transfer of carbon by this $C-CO-CO_2$ mechanism could lead to a change in direction of transfer if there was another mechanism operating whereby carbon was being lost from the crucible, i.e., if there was a carbon loss by this other mechanism at a given rate, decrease of pressure would lead to a decrease in carbon pick up by the $C-CO-CO_2$ mechanism and could thus lead to a net loss of carbon at lower pressures compared to a net gain at higher pressures.

Such a mechanism was thought possible and investigated during the static experiments. This was that carbon could be lost at low pressures through volatilization of carbon as an iron carbon compound

or as an iron carbon oxygen compound. However, as discussed, experiments done to test this proposition were negative in result.

Thus the reversal of carbon transfer with change of pressure is at present quite inexplicable.

Dynamic Conditions.

Mechanism of Reaction.

When the dynamic experiments were started consideration had to be given to the possibility that true equilibrium might not be reached when the partial pressure of CO differed from the working pressure in the tube.

For instance if the reaction

$$(FeO) + \underline{C} = \underline{Fe} + CO$$

is going to the right and reaction takes place at the slag/metal interface then CO bubbles will only be produced at a partial pressure equal to the total pressure in the tube plus the pressure due to the slag depth, that is at ~one atmosphere pressure. If it was the case that CO bubbles were being produced at pressures much higher than what was taken to be the effective CO partial pressure then γ_{FeO} values would be obtained which tended to decrease with decrease in FeO concentration. In fact the results show the opposite trend. Also, the results obtained give consistent γ_{FeO} values even when the partial pressure of CO is varied randomly by a factor of 2:1.

Since (a) equilibrium is thus obtained under the experimental conditions used, and (b) the reaction only goes in one direction to any significant extent, it is possible to postulate the mechanism of reaction under the given conditions.

Possible mechanisims for the reduction of FeO are:-

(1) The reaction procedes at the slag/metal/gas interface. That is, on the line round the edge of the slag surface where it meets the steel crucible wall.

(2) CO diffuses from the place of reaction to the gas phase through slag or metal.

(3) Carbon dissolves in the slag and reacts with gas on the slag surface.

All of these processes could allow CO to be produced at partial pressures below the total pressure of the system.

Mechanisms (1) and (2) also provide means for the reverse reaction to take place. In fact under the experimental conditions used, FeO was not produced when FeO concentration starting points below the equilibrium values were used. Since FeO would have to be produced at very low activities, i.e., in the slag, these mechanisms are the only ways in which an increase in FeO could occur. It would seem then that mechanisims (1) and (2) can only be very slow if they go at all and that reduction of FeO occurs via mechanism (3).

It has been shown in work on reaction between solid FeO containing slags and coke that carbon is soluble in lime-alumina-silica slag,(26). When a slag plug is heated in contact with coke, iron is produced in the bulk of the slag rather than at the interface. Slag, analysed for carbon, was shown to contain significant, although small, amounts. Even although the solubility is small, carbon can be expected to show a high diffusivity in slag since it is so small an atom compared to those present in the slag.

It was found that when FeO was reduced in a run, iron particles were found towards the centre of the slag surface. If iron was produced at the metal-slag interface it could be expected to attach to and take up

the orientation of the iron crystal at the interface where the iron was formed. It was also observed that there was no sign of bubble formation in the dynamic runs although bubble formation was obviously taking place in the static runs in which the working pressure and the partial pressure of CO are the same.

These observations are in line with the postulation that FeO is reduced at the slag-gas interface by carbon dissolved in the slag, thus producing CO at pressures equal to the partial pressure of CO in the gas mixture.

Philbrook and Kirkbride(19) also noted that iron formed on the surface of FeO containing slags when the iron oxide was reduced. They ascribed this effect to the carrying of iron to the slag surface by ascending CO bubbles. They stated that the amount of metallic iron found at the surface was greater than corresponded to the amount of FeO reduced. This could be the case since the slag was reduced by carbon in an iron melt which was agitated by high frequency induction heating.

In their work CO bubbles could be produced at the metal/slag interface at one atmosphere pressure since they were using carbon saturated iron to reduce FeO. In the present work there was no sign of bubble formation in the slag melt and the metal phase containing carbon was solid so it is unlikely that the mechanism given by Philbrook and Kirkbride was operating.

An attempt was made at an iron balance but the weights of constituents involved were so low that the results were inconclusive.

For the iron to stay on the slag surface in such conditions means, of course, that interfacial tensions between slag/metal, slag/gas and metal/gas phases are such as to counter the tendency for the heavier metal to fall to the bottom of the slag melt.

Slow Rate of Reaction at Low Concentrations of FeO.

It was also found in the dynamic runs that the reaction reducing FeO became very slow at low concentrations and there is evidence that FeO may even be produced at very low concentrations of FeO. At values of 0.10% FeO in the slag, and 0.4%C in the crucible, a run could be held in pure Argon for several hours with no decrease in FeO content. Even when a graphite crucible was used a four hour run only produced a drop to 0.07% FeO from 0.11% FeO.

The rather rapid change of behaviour over the range 0.13 to 0.11% FeO makes it seem likely that not only is the reaction rate falling off with concentration but that there is a slow reaction possible which produces FeO independent of CO partial pressure, since FeO is not produced at higher concentrations when a run is made with an FeO content below equilibirum. Such a reaction suggested by Taylor and Stobo(5) is the reduction of SiO_2 by Fe to produce Si in metal and (FeO) in

slag. This reaction is known to be slow and thus can only become significant when reduction of FeO by carbon becomes very slow.

The fact ~~that~~ of this practical impossibility of reduction of FeO by C in metal unsaturated with silicon - also found by Arthur (1), accompanied by the fact that low FeO values are obtained where silicon saturated metal is used (1) and (6), suggests that the reduction of SiO_2 by Fe can proceed at a significant rate when FeO concentration is reduced to the order of 0.1%.

Thus the present work supports the findings of the other workers mentioned and lends support to the postulation made by Taylor and Stobo (5), that sulphur transfer from metal to slag may be due to an interfacial mechanism and not greatly dependent on a_{FeO} of the slag when the FeO concentration drops to about 0.1%. If this is so the estimation of γ_{FeO} at very low concentrations of FeO in blast furnace type slags may not be very significant in relation to the sulphur distribution problem in the blast furnace. However, at intermediate values which may hold in the blast furnace γ_{FeO} may be of greater significance. This will be discussed more fully later. (See page 66).

Limits of FeO Concentration Range Covered by the Work.

The lower limit of the range was fixed at about 0.13% FeO for the reasons discussed in the preceding section.

The upper limit of about 1.0% FeO was established by the fact that to get higher FeO content in the slags, low carbon steels and higher CO gas mixtures would be required. However, as the CO content of the gas increases so does the rate of carburisation of the crucibles. As described in the experimental procedure it is thus difficult to get FeO values much above 1.0%.

The range could have been extended by use of CO/CO_2 gas mixtures. The reaction involved would then be:

$$(FeO) + CO = \underline{Fe} + CO_2.$$

However, as described on page 48, at low CO_2 values, carbon deposition troubles would lead to very large errors and the method was not attempted.

Effect of Slag Composition on γ_{FeO}.

The values of γ_{FeO} obtained in this work range from 0.8 to 1.2 depending on composition for FeO concentrations down to 0.6% FeO and from there rise to about 1.5 as FeO content falls to about 0.1%. The curves shown in Figs.6 and 7 indicate that γ_{FeO} is steady round about 1.0 for FeO contents from 0.6% to well above 1.2% FeO.

These results can be compared with the results obtained by Arthur(1). He obtained a rise in γ_{FeO} from 0.08 to 0.1 as FeO content fell from 1.4% to 0.3%. As in the present work his slags contained CaO and SiO_2 in ratios of about 1:1 but his slags had 40% Al_2O_3 as compared with 16-22% Al_2O_3 in the slags used here.

It would seem then that composition has a very important effect. There are two ways in which composition could affect γ_{FeO} as calculated. The first is that there is no real reason for supposing that the mole fraction can be calculated on the assumption that the molar species present are the oxides FeO, Al_2O_3, CaO and SiO_2 and not more complex molecules or ions. (See Richardson(27)). Thus a change in concentration of a constituent in a given system can alter the kind and number of species present and so make N (mole fraction) a discontinuous or changing function of concentration.

Also, of course, the activity coefficient of a constituent at any given concentration can be affected by changes in concentrations of other constituents.

The first effect could account for the change found in γ_{FeO} with concentration of FeO while the second could give rise to different γ_{FeO}

values for a given FeO content in different slags.

One effect of change of composition in silicate melts which is to be expected is that the increase in basicity will lead to an increase in activity coefficient of the base material present. Thus workers with $CaO:SiO_2$ binary slags find an increase in γ_{CaO} as the orthosilicate composition is approached from the high SiO_2 side. (See Carter and MacFarlane(28)). This effect can be explained by considering the state of dissociation of C_2S in the melt. This is a very stable compound and its degree of dissociation in a melt can be considered to be very low. Thus at compositions far to the silica side of the C_2S compositions there will be very little free lime available to act chemically as lime. As the C_2S composition is approached the amount of free lime will increase giving rise to an increase in γ_{CaO} at this composition and beyond. This is an over simplification since in such melts the proper model is more likely to be that of complex ions with some degree of association between ions of opposite sign. There is also the fact that other compounds are formed between lime and silica. However, presumably because of the very high free energy of formation of C_2S the system does show a smooth steep rise in γ_{CaO} as the orthosilicate composition is reached.

This effect is shown in more complex silicate systems. Thus MacFarlane(29) finds an increase in γ_{CaO} in CaO, Al_2O_3, SiO_2 slags as the CaO concentration is increased along lines of constatn Al_2O_3/SiO_2 ratio.

In more complex slags then it could be expected that an increase in basicity would lead to an increase in activity coefficient for any base present. This interchangeability of bases under certain conditions and for certain purposes is used in steel making slag work and its validity is indicated by the consistency of the data used by Turkdogan and Pearson(9) as shown in Fig.9.

Thus, if iron oxide at the low concentrations involved is considered as a base interchangeable with lime an increase in basicity could be expected to cause an increase in γ_{FeO}.

This effect is also indicated by the curves shown in Figs. 8 and 9, taken from Bishop, Lander, Grant and Chipman(9), and Turkdogan and Pearson(9), i.e., there is an increase in γ_{FeO} as basicity is increased from the acid side towards more basic slag compositions.

Comparison of the γ_{FeO} curve for Slag A with that for Slag B, at 1450°C shows such an increase in γ_{FeO} with increase in basicity. Slag A gives an excess base value (equal to moles CaO - moles Al_2O_3 - molesSiO_2) of +0.020 compared with -0.1 for Slag B.

Comparison of Slag A with Slag C could be expected to show the same effect since Slag C has an excess base value of -0.072. However, Slag C shows no decrease in γ_{FeO} as compared with Slag A.

However, Slag C has a significantly higher Al_2O_3 content than Slags A or B and there is evidence that at slag compositions corresponding to blast furnace slag types, increase in Al_2O_3 may lead to more basic behaviour than is indicated by taking Al_2O_3 as additive to SiO_2 when

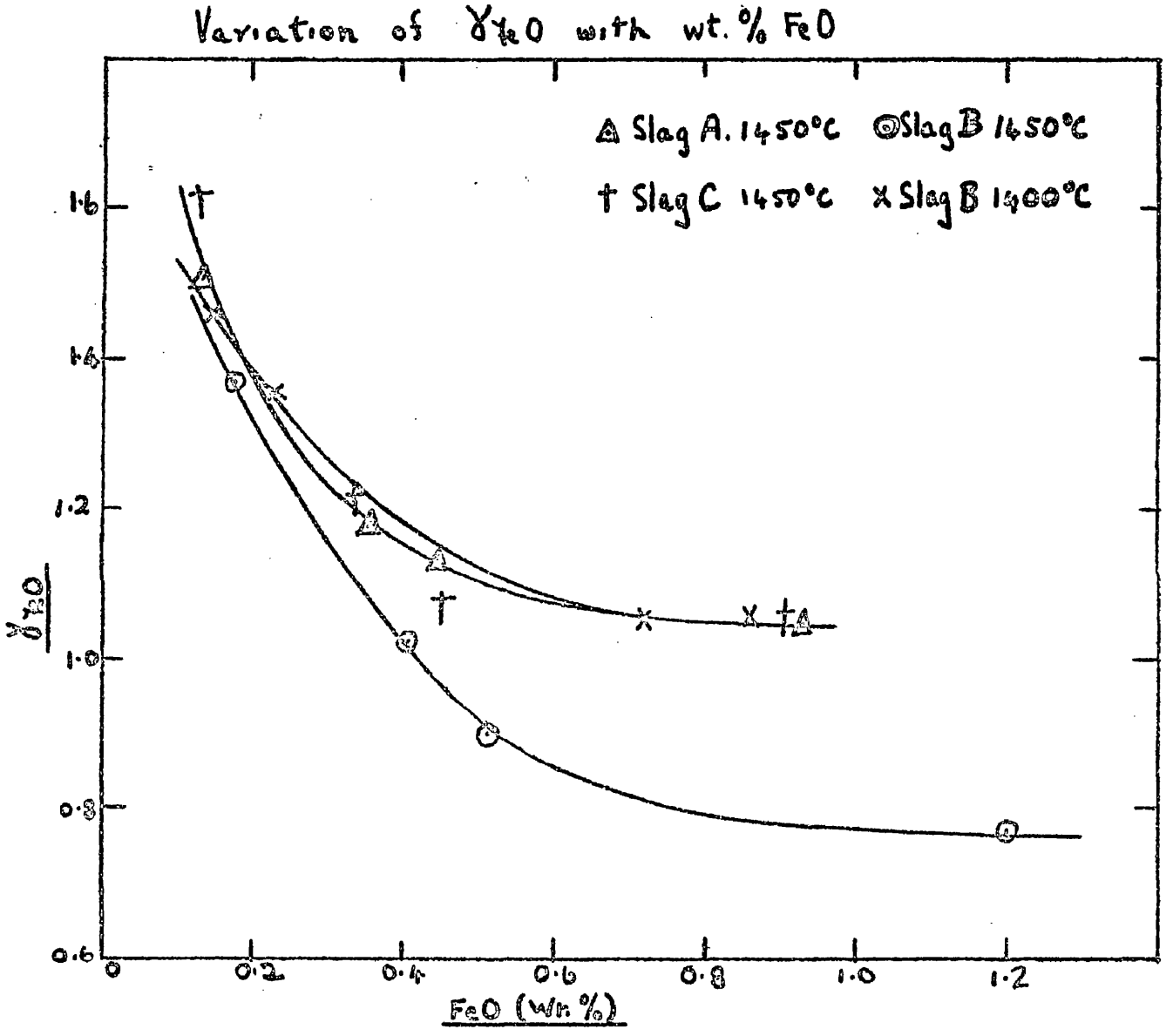
assessing slag basicity. Thus MacFarlane's(29) results show that replacement of SiO_2 by Al_2O_3 at constant lime content leads to an increase in γ_{CaO}. He attributes this to the lower affinity of CaO for Al_2O_3 than for SiO_2.

A similar effect is shown by the results of Hatch and Chipman(6). In their work on sulphur distribution between blast furnace type slags and metal they found that for slags of ~16% Al_2O_3 there was a linear relationship between an empirical expression for slag basicity [excess base = $(CaO + {}^2/_3\ MgO) - (SiO_2 + Al_2O_3)$ moles per 100 gms. slag], and the sulphur distribution ratio slag/metal. Since the sulphur distribution is proportional to the activity of lime in the slag, excess base is proportional to lime activity in these slags. Other slags containing (a) higher Al_2O_3 concentrations (20-25%), and (b) lower Al_2O_3 concentrations (~10-12%) gave higher and lower lime activities respectively. This shows that over the range considered Al_2O_3 at higher concentrations behaves in a less acid fashion than at medium concentrations and in a more acid fashion at low concentrations.

Thus in comparing Slags C with Slag A the effect of high Al_2O_3 in Slag C could cancel the effect of the lower lime content of Slag C and give similar γ_{FeO} values for the two slags.

In comparing Slag C with Slag B, they have similar lime content and excess base values as calculated by subtracting moles of SiO_2 and moles of Al_2O_3 from moles of CaO but the effect of the higher Al_2O_3 content of Slag C may cause the increase in γ_{FeO} values compared to Slag B.

Fig. 6.



Slag Compositions (Wt. %)

	CaO	Al_2O_3	SiO_2
Slag A	45.7	16.8	37.4
Slag B	40.0	18.5	41.5
Slag C	40.5	22.6	36.9

The difference between γ_{FeO} values obtained in the present work and those obtained by Arthur(1) probably lies in the very low CaO content of Arthur's slags. These slags contained 30% CaO, 30% SiO_2 and 40% Al_2O_3, and would be much less basic than the present slags which could account for the fact that Arthur's γ_{FeO} values are about 10 times smaller than the values obtained here.

There is also the possibility that in more acid slags replacement of SiO_2 by Al_2O_3 could lead to a decrease in γ_{FeO}. In a highly siliceous melt there is a tendency to two liquid formation, even if the composition is outside a 2-liquid region, because of the very strong bond between Si ions and oxygen ions in the melt. Thus an almost complete SiO_2 network or very complex silicate ions are possible in the melt leaving widely dispersed oxygen ions singly bonded to silicon ions to satisfy the valency requirement of any other cation present. To satisfy the coordination requirement of this other cation requires a greater number of these singly bonded oxygen ions per unit volume and if the foreign cation has a high oxygen bond strength there will be at least a tendency to two liquid formation, the liquid low in SiO_2 having enough singly-bonded oxygens per unit volume to satisfy the coordination needs of the added cation. Thus in a highly siliceous melt the cation could show a high activity coefficient. If SiO_2 is replaced by Al_2O_3, Al can substitute for Si in its network or in its complex ions, whichever are considered to be present in the melt. But since Al has not such a high oxygen bond strength as Si there will be less tendency for a more

basic cation such as Fe to cause two liquid formation and such a cation could be considered to be more closely associated with the alumino-silicate network or complexes. Thus it is possible that replacement of SiO_2 by Al_2O_3 in more acid melts could lead to a decrease in γ_{FeO} and in the case of Arthur's slags be an additive effect to the effect of decrease of basicity. This would help to account for the very much lower values of γ_{FeO} found by Arthur.

The effect of replacement of SiO_2 by Al_2O_3 in acid slags can be regarded in another way. There is a relation between the free energy of formation of a compound formed by two substances and the activities exhibited by these substances. Thus the free energies of formation of the compounds possible between FeO and Al_2O_3 and FeO and SiO_2 can be compared. From the data given by Richardson, Jeffes and Withers(30) it can be calculated that the free energy of formation of hercynite (-40 Cal. at 1400°C) is very much higher than that of fayalite (-5,500 Cal. at 1400°C). They also give a figure for liquid $FeSiO_3$ of the order of -2.8 Cal. at 1600°C. Thus the association between FeO and Al_2O_3 in a melt would seem to be much greater than that between FeO and SiO_2. These figures lend support to the possibility discussed above that at highly acid compositions the effect of SiO_2 replacement by Al_2O_3 may be reversed with respect to its behaviour in more basic slags and lead to a decrease in γ_{FeO}.

Comparison with Steelmaking Slag Data.

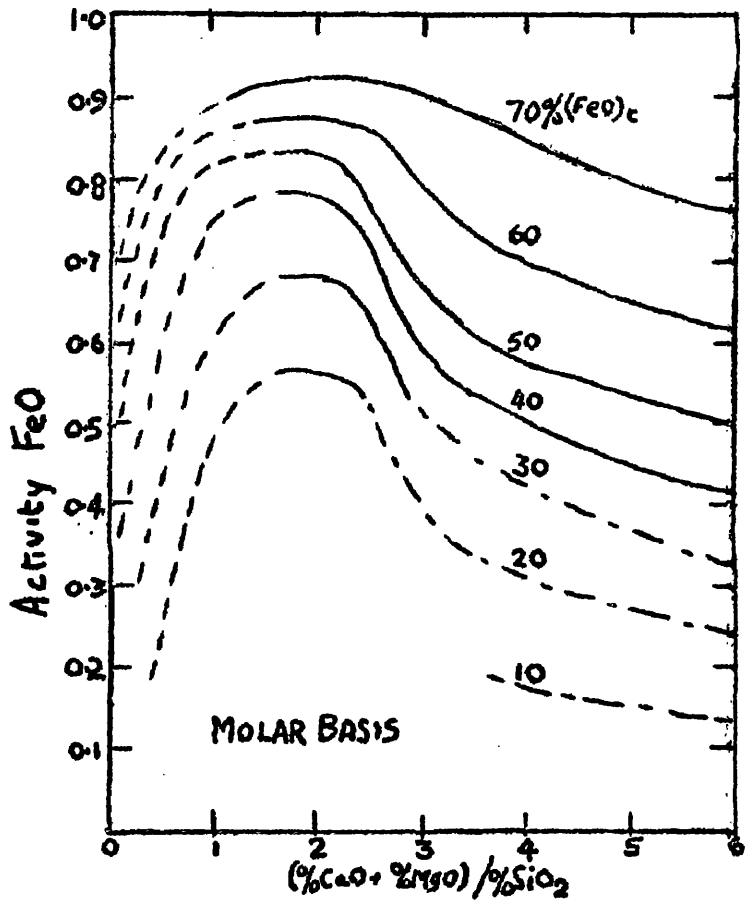
Comparison of the results obtained for blast furnace type slags with those obtained for steel making slags is made difficult by the presence in blast furnace slags of Al_2O_3. As can be seen from Figs. (8) and (9) γ_{FeO} in the steelmaking slags varies greatly with basicity. In these slags basicity ratio is taken as the $(CaO+MnO+MgO) : SiO_2$ ratio after allowance has been made for the formation of phosphates and sulphides. There is little Al_2O_3 to be allowed for. In blast furnace slags, to obtain an equivalent ratio some decision must be made about Al_2O_3, i.e., whether to regard it as neutral or whether, since it is a network former in the presence of SiO_2, to regard it as additive to SiO_2.

In Fig.8, taken from Bishop, Lander, Grant and Chipman(7), γ_{FeO} is seen to be dropping to about 1 as the basicity ratio decreases from 1.3 towards zero after being on a plateau of about 3 for basicity ratios between 2.3 and 1.3. The same effect is indicated in Fig.9, taken from Turkdogan and Pearson(9).

To make a comparison with the present work, Al_2O_3 must be considered as equated to SiO_2 and gives the slags basicity ratios of (0.8 - 1.0). Such ratios coincide with the range in Fig.(8) where γ_{FeO} is altering sharply but does give γ_{FeO} values of the same order as values found in this work. Inspection of Fig.(9) leads to a similar conclusion.

However, in both cases there is a very large extrapolation involved, i.e., from 10% FeO to 1% FeO in addition to the difficulty of allowing for the presence of Al_2O_3 in the blast furnace type slags.

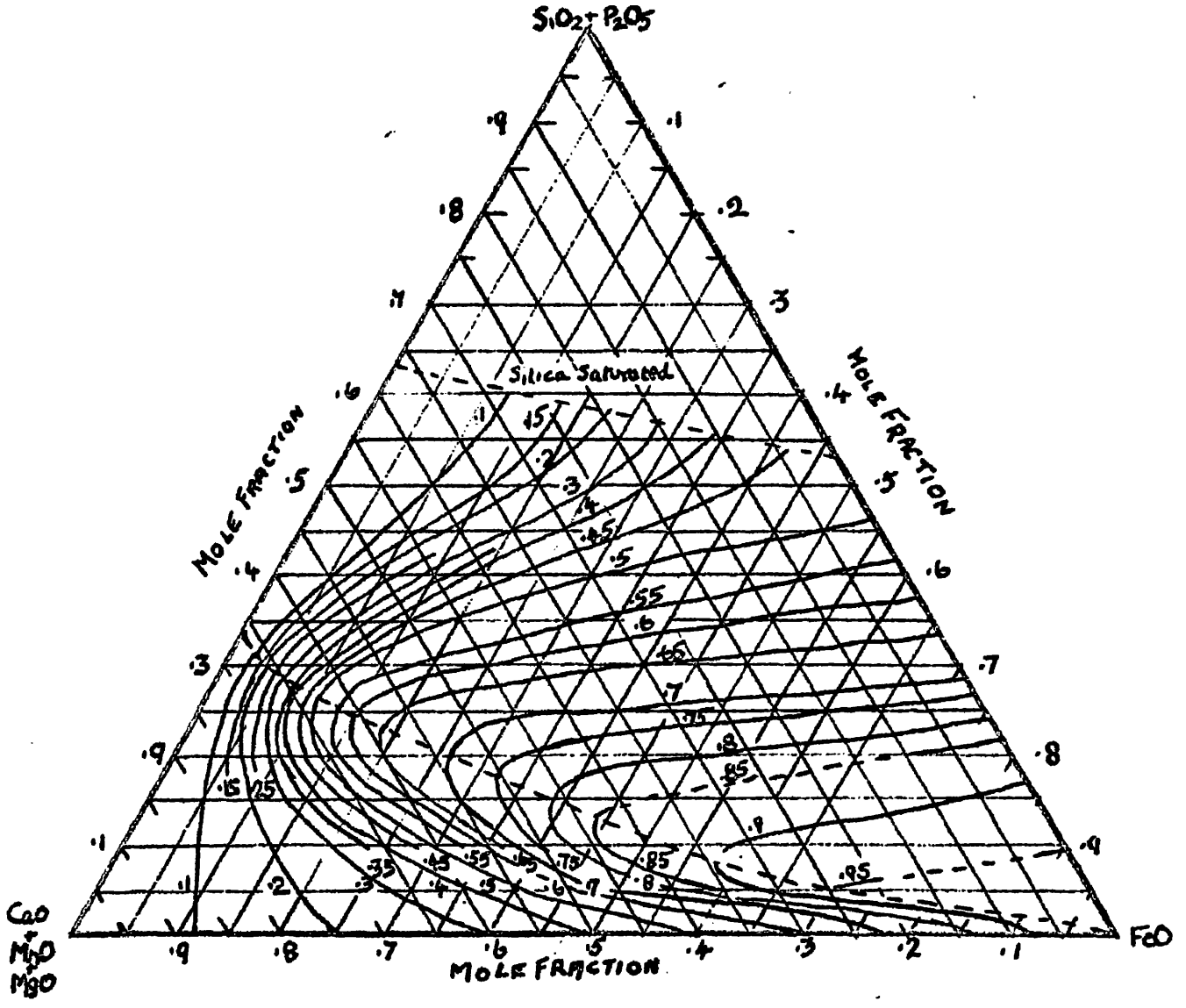
Fig. 8.



Open hearth-type slag data as summarised by H.L. BISHOP Jr, H.N LANDER, N.J. GRANT, & J. CHIPMAN.

Journal of Metals, July 1956 8 p. 862.

Fig. 9.



Activity of ferrous oxide in complex slags.

E.T. TURKDOGAN & J. PEARSON J.I.S.I. 1953 173 p917

Richardson and Jeffes(21) suggest that at 1% concentration FeO in blast furnace slags has an activity of about 0.03. This would give a γ_{FeO} value considerably higher than indicated by this work.

Effect of Temperature on γ_{FeO}.

The effect of temperature on γ_{FeO} is indicated in Fig.7 by the curves obtained at 1400°C and 1450°C for Slag B. The results suggest a decrease in γ_{FeO} with rise in temperature. M. Rey(31) estimates that in the binary system $FeO \cdot SiO_2$ the heat of mixing of any melt is not zero. Turkdogan and Pearson(9) find no temperature effect in more complex systems.

The effect of temperature in complex silicate systems is difficult to estimate. There may be a fall in γ_{FeO} due to an increasing "solubility" effect with rise in temperature or increase of temperature could cause a break down of complexes in the melt leading to a decrease in calculated γ_{FeO}. If FeO itself is p art of a complex which breaks down on heating then release of FeO in this fashion would cause a rise in γ_{FeO} with rise in t emperature. The total effect of these three possibilities is presumably variable from one composition to the other and in the present case leads to a fall in γ_{FeO} with rise in temperature.

Change in γ_{FeO} with Change in FeO Concentration.

The curves obtained for γ_{FeO} against FeO concentration (Fig.6) show that γ_{FeO} is still rising steeply at the lowest concentration of FeO covered by the experiments. Henry's Law then can only be approached at very high dilution of FeO in these slags.

The change in γ_{FeO} shown in the range covered is also shown by Arthur's results (See Page 58).

Application of Findings to Blast Furnace Operation.

The determined values of γ_{FeO} are of assistance in assessing the conditions found in blast furnace operation. As discussed in the introduction, FeO content has a bearing on sulphur and silicon distribution between slag and metal. It is important to know the relationship between the oxygen potential of the slag and the oxygen potential of carbon-carbon monoxide at 1 atmosphere, as such knowledge can lead to a decision as to whether the slag is in equilibrium with metal or gas or both or neither. γ_{FeO} values found indicate that it is unlikely that even at the lower range of reported FeO concentrations (0.2-1.0% FeO) can these correspond to equilibrium values for slag relative to carbon-carbon monoxide (1 atmos.). That is, the figure is too high at 0.2% FeO to correspond to an a_{FeO} figure of 0.024% if γ_{FeO} is of the order of 1.3 as seems likely from the present work.

It cannot be said, however, that blast furnace slags are at higher oxygen potentials than the C-CO (1 atmos.) potential because high 'FeO'

results are obtained in practice through the entrainment of metallic iron particles in the slag. These particles are difficult to separate from the slag (See Appendix).

Accurate values of γ_{FeO} in slag would give reliable estimates of slag oxygen potential. Such data could be compared with the oxygen potential indicated by sulphur distribution ratios found in practice and thus lead to a decision as to whether or not blast furnace slag is in equilibrium with the metal.

Taylor and Stobo(5) obtained a measure of the slag oxygen potential relative to the oxygen potential of carbon-carbon monoxide (1 atmos.) from data on the manganese distribution between metal and slag. As they point out, this ratio is very temperature dependent and since it is difficult to get accurate temperature readings of slag and metal in the blast furnace to correspond with the slag and metal samples taken, their assessment of slag oxygen potential by this method is unreliable. They found, however, that the Mn distribution ratio indicated a slag oxygen potential 2 to 3 times as high as the oxygen potential of carbon-carbon monoxide (1 atmos.). The corresponding ratio between sulphur distribution between slag and metal in practice to that corresponding theoretically with an oxygen potential equal to that of C-CO (1 atmos.) was about $1/3$. That is their analysis of the data indicates a possibility that slag and metal are in equilibrium.

However, since FeO/Fe distribution is less temperature dependent, accurate analysis of FeO combined with a knowledge of γ_{FeO} in blast

furnace slags is the best hope of an accurate assessment of slag oxygen potential.

Although there is a possibility that the slag oxygen potential is 2 to 3 times that corresponding to carbon-CO (1 atmos.) the lowest reported value of 0.2% FeO is still too high to be true since for a γ_{FeO} of 1.0, the activity of FeO corresponds to an oxygen potential about 10 times that of carbon - CO (1 atmos.).

The suggested mechanism for the reaction investigated in this work may have a bearing on blast furnace practice. In discussing the relationships between slag, metal and gas phases in the blast furnace there is doubt as to the effective pressure of CO in the furnace.

In considering reactions between slag and metal where CO is produced, if the CO is considered to be produced at the slag-metal interface the effective CO pressure should be that of the working pressure at the foot of the furnace. In modern blast furnace practice this would mean something over 2 atmospheres.

Thus, if the slag oxygen potential is 2 to 3 times the oxygen potential of carbon-carbon monoxide (1 atmos.) it may be in equilibrium with the gas phase, i.e., with C-CO (2 + atmos.).

An alternative view is that the effective CO pressure is the partial pressure of CO at the foot of the furnace (= concentration of CO x pressure = 0.4 x 2+) which is thus something under 1 atmos. In view of the slowness of the reaction, FeO reduced by C to Fe, the first view

is unlikely but it has always been difficult to suggest a mechanism whereby the alternative could hold, wherein CO is produced at 1 atmos. pressure.

This problem is similar to the one encountered in the present work and the explanation given here may also apply to blast furnace conditions. i.e., carbon in solution in the slag reacts with slag oxides such as FeO and MnO at the surface of the slag and CO is thus produced at the partial pressure of CO prevailing in the furnace.

SUMMARY AND CONCLUSIONS.

SUMMARY AND CONCLUSIONS.

The equilibrium between carbon in solid iron, ferrous oxide in lime-alumina-silica slags and carbon monoxide has been investigated and values of γ_{FeO} estimated for ferrous oxide concentrations between 0.1 and 1.0%.

The range of FeO concentration was limited at the lower end by the slowness of the reaction as discussed on page (55).

The upper limit was set by the carburising effect of high CO gas mixtures as discussed on page (57).

The range could have been extended to higher FeO values by using CO/CO_2 gas mixtures and establishing equilibrium in the reaction

$$FeO + CO \simeq \underline{Fe} + CO_2$$

However, as discussed on page (48) large errors will arise with low CO_2 concentrations in such a gas mixture. Schuhmann and Ensio(11) found that at low concentrations of CO_2, carbon deposition interfered with their work and made it difficult to work with CO_2 concentrations below 12% CO. This means that there is gap between $\sim$40% and $\sim$1.0% FeO which cannot be covered satisfactorily using the above reaction or the reaction used in the present work.

Perhaps the most important conclusion to be drawn from this work then is that in reactions involving iron and CO at high temperatures interference due to the carbon deposition reaction is almost impossible

to avoid. This is probably due to the volatilisation of iron at high temperatures and its condensation in cooler parts of the reaction system thus providing a catalyst for the carbon deposition reaction.

Only under rather restricted conditions such as in Schuhmann and Ensio's work and in the present work can this interference be kept down to insignificant proportions.

This means that thermodynamic studies in the iron carbon system based on the reaction $C + CO_2 = 2CO$ are of very restricted application and casts very grave doubt on some of the work which has been done based on such reactions.

The γ_{FeO} values obtained have been compared with steel making slag data. Although there is a large extrapolation involved and there is difficulty in estimating comparable basicities for iron-making slags, the results are in reasonable agreement with such data.

The effect of slag composition variation on γ_{FeO} has been considered. It is found to decrease with decrease in slag basicity and increase with increase in alumina content.

It seems possible that in very acid slags which are high in alumina the effect of increase of alumina is reversed and leads to a decrease in γ_{FeO}.

γ_{FeO} in the slags used was found to fall with increase in temperature.

γ_{FeO} was still rising at the lower end of the range investigated (0.12% FeO) so that Henry's Law can only be approached at fairly high dilution.

A mechanism for the reaction:

$$(FeO) + \underline{C} = \underline{Fe} + CO$$

under the experimental conditions used, has been suggested. The reaction was found to proceed only to the right under these conditions.

The reaction was found to be very slow at ferrous oxide concentrations below 0.12% and it is possible that at low concentration of ferrous oxide, ferrous oxide is produced by the slow reaction:

$$SiO_2 + \underline{Fe} = \underline{Si} + (FeO)$$

The significance of the results with regard to blast furnace practice has been discussed, in particular, in relation to slag oxygen potential control and the possibility of equilibrium existing between slag and metal and slag and gas.

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APPENDIX.

A P P E N D I X.

Attention has been drawn to the difficulty of analysing slags for iron oxide when iron has been produced from such slags by reduction.

This is a difficulty encountered both in blast furnace slag analysis and in experimental work and it arises wherever metallic iron occurs in suspension in the slag. If the iron particles are very fine it is difficult to reduce the slag to a fine enough size to permit of metallic iron removal by magnet since, if grinding is taken too far, metallic iron may be oxidised in the process.

This difficulty is greatest where sulphur is present in both slag and metal(1),(2),(3). In its absence it is usually possible, by suitable grinding and use of a magnet, to get reasonably accurate results but satisfactory separation in this way has been found to be impossible in the presence of sulphur, presumably because iron is more finely disseminated throughout sulphur bearing slags.

Many attempts have been made to surmount this problem. As it was thought there might be some trouble with the FeO analysis in the present work, an effort was made to find a suitable method for separating metallic iron from the slags to be used.

Although this attempt was unsuccessful and fortunately, it was found that in the absence of sulphur magnetic separation was satisfactory,

it is felt that an outline of what was done might be of assistance to others who come upon the problem.

The method adopted was the removal of metal iron as a volatile chloride. This technique has been used in non-metallic inclusion work to obtain such inclusions, free of metal, for analysis.

Attack by chlorine converts iron to ferric chloride and this chloride can be volatilised off at temperatures above 300°C.

The higher the temperature used, the more efficiently is the iron removed but the greater the chance of attack on the non-metallic phase. In particular, iron oxide may be attacked at temperatures little greater than 300°C.

Klinger and Koch(4) developed a technique to keep attack on the non-metallic phase to a minimum. Here, the sample is held in a reaction vessel which is pumped down to $\sim 10^{-3}$ mm. of Hg. pressure. Chlorine gas is admitted at atmospheric temperature and pressure and the temperature raised to 250°C. The vessel is then pumped out again to 10^{-3} mm. of Hg. pressure, and the chlorides formed volatised off at any desired temperature.

This technique was tried using a fused silica flask to hold the sample and polyvinyl chloride tubing for connections.

The samples were made up by adding fine iron filings to ground slag to give 0.5 to 1.0% iron in the mixture. In some of the samples iron oxide was present in the slag phase to about 0.5% and in others the slag was free of iron oxide.

2 or 3 gms. of mixture was used for each run and the volatilisation temperature ranged between 350°C and 400°C.

It was found impossible to remove the small amount of metallic iron present in the mixtures.

The method presumably is satisfactory for non-metallic inclusion work where a large mass of metal has to be removed leaving a very small non-metallic residue. If this residue is contaminated by traces of metallic iron which cannot be removed no great inaccuracy arises. However, it is this last trace of iron which it is most important to remove in preparing an iron bearing slag for analysis for FeO and which cannot be taken off by the chlorination method described.

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A C K N O W L E D G M E N T S.

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